

Synthesis of aluminum isopropoxide from aluminum dross

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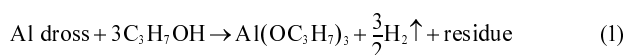
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Abstract—Synthetic reaction of aluminum isopropoxide, which is used as a starting material for catalytic-grade alumina, has been studied in the presence of a small amount of HgI₂, HgCl₂, I₂ or FeCl₃ from aluminum dross. It was synthesized by solid-liquid reaction between the aluminum metal and isopropyl alcohol, using vacuum distillation process. The purity of the synthesized aluminum isopropoxide was obtained over 97.6% experimentally, which had been analyzed quantitatively by complexometric method. The initial amount of sodium, which directly affects the catalytic activation in the alumina catalyst, was in the range of 0.926 to 1.563 wt% in the aluminum dross. Finally, it was decreased to 0.007 wt% in the aluminum isopropoxide product. Yield was changed according to the amount of aluminium existing in the aluminum dross. Aluminum could mostly be recovered regardless of the amount of aluminium existing in the aluminum dross.

Key words: Aluminum Dross, Aluminum Isopropoxide, Solid-liquid Reaction, Vacuum Distillation, Na Content

INTRODUCTION

Aluminum dross is a byproduct formed by surface oxidation of aluminum metal in the process of aluminum can recycling. It contains a considerable amount of aluminum metal component, but is usually dealt as a common solid waste and landfilled in soil. Accordingly, it brings about an increase of landfill cost and waste of valuable metal resource. For the purpose of reducing the amount of solid waste and reusing the valuable metal components, aluminum isopropoxide has been synthesized from the aluminum dross as shown in Eq. (1).



Aluminum alkoxides have been used as catalysts and as intermediates in a variety of pharmaceutical and industrial processes. They can be synthesized from various aluminum alkoxides compounds according to the type of bonded alcohol groups. e.g., aluminum ethoxide (Al(OC₂H₅)₃), aluminum isopropoxide (Al(OC₃H₇)₃), aluminum sec-butoxide (Al(OC₄H₉)₃). Among these aluminum alkoxides, aluminum isopropoxide is well known and widely used as a selective reducing agent for aldehydes and ketones. In particular, it has been widely used as a starting material for the preparation of alumina, which are directly obtained by hydrolysis of aluminum isopropoxide [Yoldas, 1975; Yoo et al., 1997, 1998]. Therefore, the aluminum isopropoxide, which is used as a starting material for the synthesis of catalyst-grade γ -alumina (γ -Al₂O₃) and boehmite (γ -AlO(OH)), was selected for the purpose of industrial usage in this

study. It is not only low in cost, but also easy to handle among the various aluminum alkoxides. The boehmite can be prepared from hydrolysis of the aluminum isopropoxide. And γ -alumina can easily be manufactured by the calcination of the boehmite.

There are many impurities such as Mg, Si, Ca, Mn, Cu, Pb, Na, Cr, Zn, Ti and O in the aluminum dross. Therefore, the aluminum isopropoxide must be recovered and be purified selectively through the vacuum distillation over the range of the boiling temperature of the aluminum isopropoxide (142 °C). Among the impurities, Na content is the most important factor of the catalytic activation for the γ -alumina catalyst. e.g. catalyst-grade (<0.1%), adsorbent-grade (<0.5%) [Kim et al., 2004]. Therefore, it is essential to minimize the amount of Na in the aluminum isopropoxide for the preparation of highly activated γ -alumina.

THE STRUCTURE OF ALUMINUM ISOPROPOXIDE

Mehrotra [1954] found that the aluminum isopropoxide was dimeric in the vapor state. Further association among these dimeric units is possible in the primary alkoxides, but the strength of the bonds appears to be weak. Assuming that the freshly distilled or sublimed alkoxide is initially dimeric structure, then the ageing effect will be due to a structural rearrangement as the aluminum realizes its maximum coordination number namely, octamers with 6 coordination. Mehrotra has demonstrated an ageing effect that the degree of polymerization increases with time.

According to Bradley [1958], the coordination number of the primary aluminum isopropoxide increased from 4 to 6, and the molecular weight increased slowly. The aluminum isopropoxide would finally involve the formation of octamers in which aluminum is entirely 6-coordinated.

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EXPERIMENTAL

The aluminum isopropoxide, which was synthesized from aluminum dross, was prepared from the solid-liquid reaction between the aluminum metal in the aluminum dross and isopropyl alcohol under the presence of a small amount (10^{-3} mol of catalyst per mol of Al) of catalyst such as HgI_2 , HgCl_2 , I_2 , or FeCl_3 . This solid-liquid reaction was maintained at the conditions that temperature is at boiling point of isopropyl alcohol and the stirring velocity is 1,000 rpm. The aluminum dross and a catalyst were simultaneously added in the reactor after isopropyl alcohol was heated in advance.

After the solid-liquid reaction between the aluminum dross and isopropyl alcohol was completed, aluminum isopropoxide was recovered and purified by vacuum distillation from the solution. If a little amount of water or air penetrates into the reactor during the vacuum distillation, side-products such as $\text{AlO}(\text{OH})$, $\text{Al}(\text{OH})_3$ could form. Therefore, it is important to prevent water or air from penetrating into the reactor.

The mole ratio of alcohol per Al added 3 mol $\text{C}_3\text{H}_7\text{OH}$ /mol Al in the reactor. The solid-liquid reaction proceeded under the condition of N_2 purging in order to prevent penetration of H_2O and remove the H_2 gas formed from the reaction. A catalyst such as HgI_2 (Fluka, >99.0%), I_2 (Fluka, >99.5%), HgCl_2 (Fluka, >99.5%) or FeCl_3 (anhydrous, Fluka, $\geq 98\%$) was used to derive the fast solid-liquid reaction. The role of the catalyst has not been understood completely until now, but it is known that the catalyst might merely clean the surface or form intermediate derivatives such a chloride, an iodide or a mercury amalgam that could react alcohols more readily [Bradley et al., 1978]. The amount of catalyst added was a small amount of 10^{-3} mol catalyst/mol Al to the reactor.

There were many impurities in the solution after the solid-liquid reaction. After the solid-liquid reaction had been completed, the solution had various impurities in it. Therefore, vacuum distillation was adopted in order to recover pure aluminum isopropoxide from the solution with many impurities. During the vacuum distillation, unreacted isopropyl alcohol was firstly distilled from the solution. Then aluminum isopropoxide was recovered and purified from the solution at the condition of 140 °C or more. The vacuum distillation process proceeded to the closed system in order to prevent the formation of aluminum hydroxide ($\text{Al}(\text{OH})_3$) by the penetration of water or air into the apparatus. The primary phase of aluminum isopropoxide obtained by the present vacuum distillation process was colorless, transparent and molten liquid phase. Then the primary phase was finally converted to white-solid phase supercooled through the progression of slow crystallization in the glove box.

PURITY ANALYSIS

The purity analysis of synthetic aluminum isopropoxide was performed by the procedure of the following two complexometric methods.

1. Wänninen-Ringbom Method

An excess (10 ml) of EDTA (2Na) solution (Ethylenediaminetetraacetic acid disodium salt solution ($[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{Na})\text{CH}_2\text{CO}_2\text{H}]_2$), 0.0501 M in water, volumetric standard, Aldrich) is added to 5 ml sample solution containing about 0.250 g aluminum isopropoxide per 50 ml acidic solution, and the pH is adjusted to 4.5 with buffers

(acetic acid-ammonium acetate (Reagent grade, Aldrich)). The sample solution is boiled for a short time, cooled, and diluted with its own volume of ethanol. 2 ml of indicator (0.25 g dithizone/methyl alcohol) is added for each 100 ml and the back-titration with zinc sulphate solution (ZnSO_4 , 0.0491 M in water, volumetric standard, Aldrich) is begun. The end-point is recognizable by a very sharp colour change from a greenish violet to red. The standard material for the aluminum source in this complexometric titration was aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$, 99.99%+, Aldrich) of high purity grade [Wänninen and Ringbom, 1955]. The standard material for the aluminum analysis in this complexometric titration was a high purity-grade aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$, 99.99%+, Aldrich) [Wänninen and Ringbom, 1955].

2. Xylenol Orange Method

The sample solution is prepared as in a previous description. The pH is adjusted to 5.4 with buffers (acetic acid-sodium acetate (Reagent grade, Aldrich)). The sample solution is heated by mantle for a few minutes, cooled, added 1 g of hexamine (Hexamethylenetetraamine, >99.5%, Riedel-deHaën) and added 1 ml of 0.03% Xylenol orange indicator (GR. Daejung Chemicals & Metals Co.). The back-titration with lead nitrate solution ($\text{Pb}(\text{NO}_3)_2$, 0.0500 M in water, 99.99%, Aldrich) is begun. The end-point is recognizable by a very sharp color change from a light orange to pink [Brady and Gwilt, 1962].

RESULTS AND DISCUSSION

The aluminum dross is a byproduct being formed by surface oxidation of aluminum metal in the process of aluminum can recycling and is a very stable state. Accordingly, it is necessary to calcine the aluminum dross for the purpose of reacting effectively the solid-liquid reaction between aluminum dross and isopropyl alcohol. The calcination temperature is suitable for the range of 300 to 600 °C for the purpose of removal of organic impurities existing in the aluminum dross and softening of metal component. If it is higher than 600 °C, the aluminum metal existing in the aluminum dross would be dissolved and transformed to the aluminum bulk. This aluminum bulk could not easily be reacted with isopropyl alcohol. Therefore, the pretreatment temperature must be maintained at the condition of less than 600 °C and of reduction inflowing N_2 gas for the prevention of the Al oxidation with air and the generation of volatile gases from the aluminum dross.

The pretreated aluminum dross proceeded to the solid-liquid reaction with isopropyl alcohol in the presence of such a catalyst as HgI_2 , I_2 , HgCl_2 or FeCl_3 . Generally, the aluminum dross contains a lot of aluminas and various metal components such as Cu, Mg, Si, Ca, Mn, Cu, Pb, Na, Cr and Zn. It is very important to separate these aluminas and various metal components in order to obtain pure aluminum isopropoxide from the solid-liquid reacted solution. Accordingly, vacuum distillation was carried out for the purpose of this separation of pure aluminum isopropoxide.

In this experiment, the time of solid-liquid reaction took from 11 to 120 hours according to the type of catalysts. It took about 11 to 12 hours in the case of HgI_2 , I_2 , HgCl_2 , but 120 hours in FeCl_3 . The reaction time was shown to be in order of $\text{HgI}_2 < \text{I}_2 < \text{HgCl}_2 < \text{FeCl}_3$ at this experimental condition.

Synthetic yield was changed according to the Al content existing in the aluminum dross. As a result, the yield recovered was about

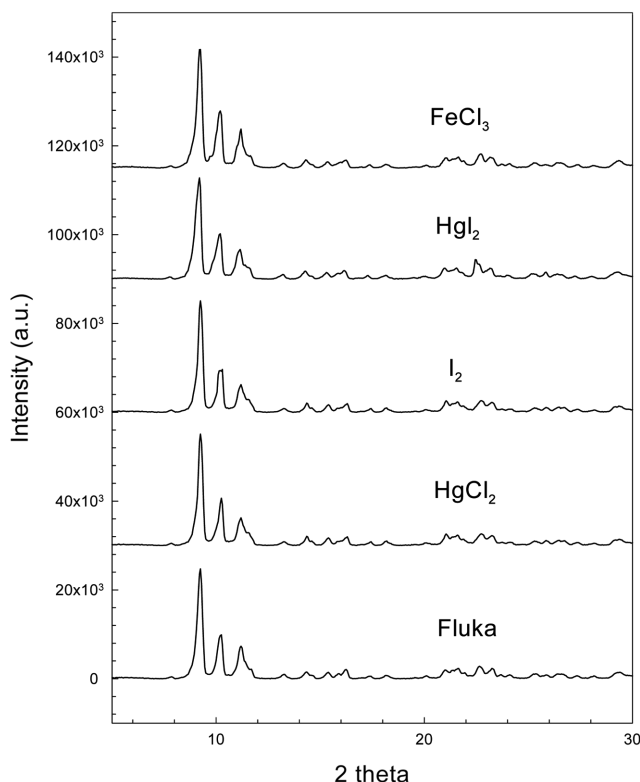


Fig. 1. XRD patterns of commercial aluminum isopropoxide and synthesized aluminum isopropoxides.

50% in the case of the aluminum dross with 50% Al and about 20% in the case of the aluminum dross with 20% Al. Accordingly, the yield of the aluminum isopropoxide has changed to the Al content existing in the aluminum dross. Aluminum component existing in the aluminum dross could mostly be recovered through the present synthetic apparatus and method regardless of the amount of existing Al.

Crystallinity of the synthesized aluminum isopropoxide was carried out under the following analytical condition (CuK α Filter, scanning speed 5°/min, 30 kV, 20 mA, 10° \leq 2 θ \leq 90° scanning range) by X-ray diffraction analyzer (Rigaku). As shown in Fig. 1, XRD peaks of the synthesized aluminum isopropoxide and commercial aluminum isopropoxide, were the same as crystal structure and crystallinity.

The type and amount of bonding group in the aluminum isopropoxide was analyzed in the range of 800-3,750 cm⁻¹ wavelength number by Liquid FT-infrared analyzer (FTS-60, BIO-RAD). The FT-IR result was obtained as shown in Fig. 2. Where, the synthesized aluminum isopropoxide was dissolved by CCl₄ solvent in the glove box to avoid contact with water in the air. The aluminum isopropoxide solution dissolved by CCl₄ could avoid a side reaction with water in the air. By this reason, the liquid FT-infrared analyzer was used in order to know the type and amount of aluminum isopropoxide bonding groups quantitatively. Absorption peaks of the aluminum isopropoxide synthesized in this experiment showed that it was the same thing of the aluminum isopropoxide of Fluka. Commonly, the characteristic peak of Al-O-C bond appears at 1,033 cm⁻¹. Other absorption peaks indicate characteristic peaks of isopropyl alcohol. Especially, the wide peak of 3,400 cm⁻¹ was the peak of

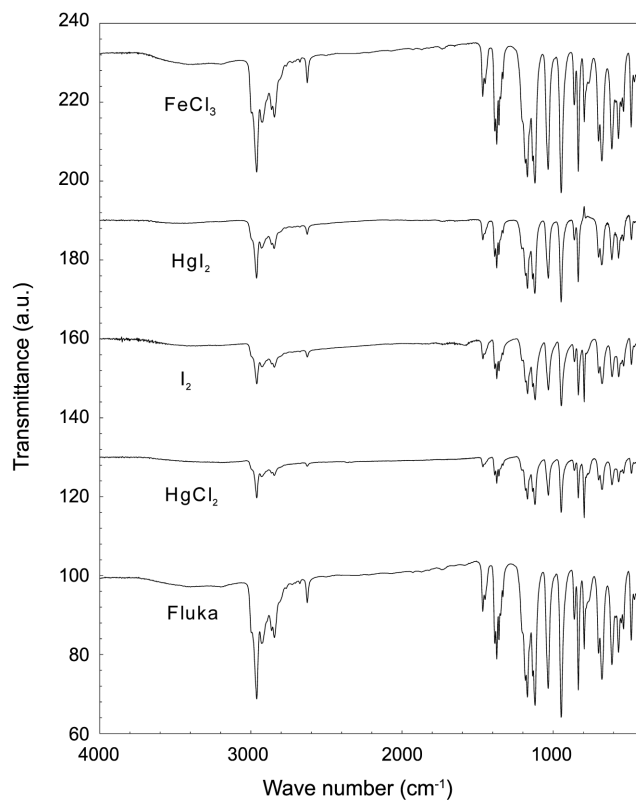


Fig. 2. FT-IR curves of commercial aluminum isopropoxide and synthesized aluminum isopropoxides.

H₂O adsorption. Accordingly, we could ascertain that the aluminum isopropoxide was successfully synthesized in this experiment.

The aluminum isopropoxide can be synthesized under the condition of no catalyst, but the reaction rate is very low in that case. Accordingly, it is essential to use a catalyst such as HgCl₂, I₂, FeCl₃, FeCl₂, SnCl₄, titanium carboxylate, gallium, indium and finely divided alumina in order to increase the reaction rate. Based on the preliminary experiment, the catalysts such as HgI₂, HgCl₂, I₂ or FeCl₃ were finally selected in this study. Primary phase of the aluminum isopropoxide was obtained by vacuum distillation with the condition of 145-150 °C and 5 mmHg. At this time, the mercuric component as a catalyst has the pollution of heavy metal in the residue of aluminum dross. Therefore, I₂ and FeCl₃ are in a better position as a catalyst in this aspect. On the other hand, FeCl₃ catalyst is very low in the catalytic activation. Based on the previous descriptions, it is very important to optimize various process variables such as catalytic volatility, yield, purity, explosiveness, formation of aluminum oxide and hydroxide in the product, simplification of process and prevention of inflow of air or oxygen into the reactor.

This study was particularly focussed on the investigation of the effect of the type of catalyst and reaction condition in order to obtain aluminum isopropoxide with a high yield and purity. The temperature of the solid-liquid reaction was controlled on the level of boiling point of isopropyl alcohol, and the reaction pressure proceeded at atmosphere. The experiment must particularly be given attention because the production of H₂ gas and reaction heat in the dissolution reaction have the risk of reactor explosion. Accordingly, the ventilation of N₂ gas in the reactor is particularly important to

Table 1. Purity of aluminum isopropoxides synthesized from various catalysts

Catalysts	Purity (%)
AIP (Fluka, >97%)	97.55
HgI ₂	98.00
I ₂	97.60
HgCl ₂	97.65
FeCl ₃	98.23

prevent the risk of explosion and penetration of H₂O. If H₂O penetrates into the reactor, aluminum hydroxide is formed by hydrolysis between H₂O and aluminum isopropoxide. As a result of purity analysis by two complexometric titrations, the purity of commercial aluminum isopropoxide (Fluka, >97% purity) was 97.55% and the purity of the synthesized aluminum isopropoxide was over 97.60% regardless of used catalysts as shown in Table 1.

Powder phase of commercial aluminum isopropoxide and synthesized aluminum isopropoxides was observed in the results of Fig. 3(a)-(e) by SEM. In the case of commercial aluminum isopropoxide of Fluka ($\geq 97\%$, Fluka), the photograph shows heterogeneous aggregated powder phases. Aluminum isopropoxides synthesized by using HgI₂, HgCl₂, I₂ catalysts, show powder phases with uniform shapes, but aluminum isopropoxide synthesized by using FeCl₃ catalyst, shows heterogeneous aggregated solid powder phase like commercial aluminum isopropoxide.

There were many impurities such as Mg, Si, Ca, Mn, Cu, Pb, Na, Cr, Zn, Ti and O in the aluminum dross used as a raw material. Impurity content in the aluminum dross and in the synthesized aluminum isopropoxide was estimated by quantitatively using ICP (Inductively coupled plasma, GBC, Integra XL dual Mono). As a result of ICP analysis, impurities such as Mg, Si, Ca, Mn, Cu, Pb, Cr, Zn,

Table 2. Comparison of sodium content in the aluminum dross and aluminum isopropoxides synthesized from various catalysts

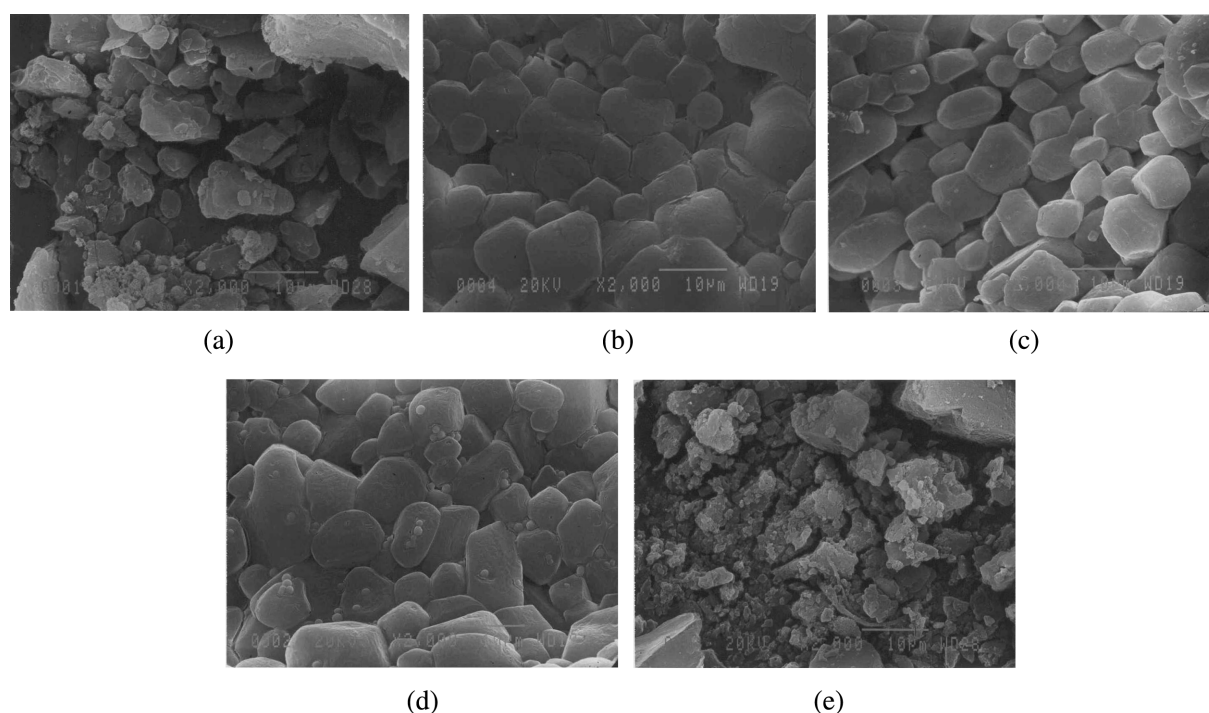
Catalysts	Na (wt%)
Al dross (bulk-granules)	0.926-1.563
HgI ₂	0.007
I ₂	0.007
HgCl ₂	0.007
FeCl ₃	0.007

Ti in the aluminum isopropoxides obtained after vacuum distillation were never found.

Commonly, the 0.1 wt% of Na component is the basis of criterion for the alumina with high purity and high activation. Table 2 is a result of Na content existing in the aluminum dross and in the synthesized aluminum isopropoxide by ICP. As a result of the present analysis, Na content has decreased from the range of 0.926 to 1.563 wt% in the initial aluminum dross to 0.007 wt% in the synthesized aluminum isopropoxide. Therefore, the aluminum isopropoxide synthesized in the present experiment is available as a starting material for the alumina with high purity and with high activation. Based on the results, this synthetic method could selectively recover all aluminum component contained in the aluminum dross.

CONCLUSION

Aluminium isopropoxide has been synthesized from aluminum dross and isopropyl alcohol. The reaction was performed through a solid-liquid reaction and a vacuum distillation. The initial aluminum isopropoxide had a colorless transparent solution phase with a dimeric structure but it was transformed into a white-solid powder phase

**Fig. 3. Powder phase of aluminum isopropoxides on various catalysts; (a) commercial (b) HgCl₂ (c) HgI₂ (d) I₂ (e) FeCl₃.**

with a octameric structure. HgI_2 , I_2 , HgCl_2 or FeCl_3 have been used as a catalyst for increasing the solid-liquid reaction rate. It took about 11 to 12 hours in case of using HgI_2 , I_2 , HgCl_2 but 120 hours in FeCl_3 as a catalyst, respectively. It was found that solid-liquid reaction rate was in order of $\text{HgI}_2 > \text{I}_2 > \text{HgCl}_2 > \text{FeCl}_3$. Finally, the aluminum isopropoxides with a 97.60% purity were synthesized by using the above catalysts.

In the aluminum dross, there were many impurities such as Mg, K, Ca, S, Cl, O, Al_2O_3 in addition to Al. But no impurity was found in this synthesized aluminum isopropoxide. Especially, the aluminum isopropoxide had a 0.007 wt% sodium content, which could be catalyst-grade. Accordingly, this aluminum isopropoxide would be available for a starting material in order to make a high purified and activated alumina.

Synthetic yield of aluminum isopropoxide has changed according to the aluminum ratio in the aluminum dross, e.g., 50%, 20%. Finally, the aluminum component could be mostly recovered from the aluminium dross.

The production cost of aluminum isopropoxide could be diminished to about 10%, in comparison with the price of commercial aluminum isopropoxide. Based on the above results, this study would be expected to contribute to the spread of the various alumina product such as a catalyst-grade activated alumina, a high purity alumina.

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