Synthesis of aluminum ethoxide from used aluminum cans

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Abstract−Aluminum ethoxide (AE) was synthesized to a high purity grade through dissolution reaction and vacuum distillation from used Al cans (UACs) under the condition of 3 mol C_2H_5OH/mol Al of stoichiometric ratio. 10^{-3} mol HgI_2/mol Al as a catalyst and 0.5 mol xylene/mol Al as a solvent for the control of reaction temperature were added. The UACs were cut into small pieces and heat-treated at the condition of 600 °C to remove impurities from UACs. Using the pretreated UACs, the high purity AE was synthesized and analyzed quantitatively by a complexometric method. The results of our experiment revealed that the reaction gives a 99.1% purity and 75% yield corresponding to the total amount of Al existing in the pretreated UACs.

Key words: Used Aluminum Cans (UACs), Aluminum Ethoxide, Dissolution Reaction, Vacuum Distillation, High Purity

INTRODUCTION

Aluminum (Al) cans are one of the most common items in the packaging industry. More than 80% of Al in the municipal solid waste is from UACs, and the remaining 20% consists of items such as Al foil, flexible packaging, appliances, and furniture. Since the majority of Al found in the municipal solid waste is in the form of UACs, recycling efforts should focus on the recovery of this form of packaging. Increased concerns by the public regarding the environment, including concerns over decreasing landfill capacity, littering, and increasing energy prices, have caused Al can recycling to steadily increase over the past two decades. This recycling not only saves valuable landfill space, but also minimizes energy consumption during the manufacture of Al products. Manufacturing new Al cans from UACs uses 95% less energy than producing them from virgin materials, an energy savings equivalent to tens of millions of barrels of oil each year [1].

In the process of conventional Al can recycling until now, the collected UACs are cut into small pieces, washed, dried, melted down and finally formed into Al sheets to be utilized in the manufacture of new cans. The upper surface layer of the molten Al solution is oxidized to the alumina by water and oxygen in air in the process. The oxidized surface layer is called as "Al dross". In general, the yield is diminished to 20-30% because of the formation of the Al dross.

Al alkoxide has various types of compounds such as aluminum ethoxide (AE, $Al(OC_2H_5)_3$) [2], aluminum isopropoxide (AIP, Al $(OC_3H_7)_3$) [3-5], aluminum sec-butoxide (ASB, $Al(OC_4H_9)_3$) [6,7] depending on the bonded alcohol groups. Among these Al alkoxide compounds, AE has been used as a starting material in various fields like catalyst, composite material and pharmaceutical industry. AE has also been a catalyst in preparing biodegradable polyes-

ter or in producing ethyl acetate by the Tischenko condensation of acetaldehyde [8]. Because of high price of alkoxide materials, however, it has not been used widely in the industries.

These approaches of the Al alkoxide from UACs are very favorable from the viewpoint of an effective resource recycling and high value-added applications. Furthermore, this synthetic technology could completely escape the formation of Al dross as a side product.

In previous studies, we have examined the synthesis of AIP from Al dross [9,10] and dissolution kinetics of the aluminum can in isopropyl alcohol for the synthesis of AIP [11]. The price of AIP with an extra pure grade is about 100,000 won/kg and ASB is about 70,000 won/kg. On the other hand, The AE with an extra pure grade is on sale at the price of about 1,600,000 won/kg, the highest price in the Al alkoxide compounds because of the difficulty of synthesis. Therefore, we selected the AE from UACs as a research target.

The AE compound is synthesized at the presence of catalyst by the following stoichiometric Eq. (1).

$$Al_{can}(s) + 3C_2H_5OH(l) \rightarrow Al(OC_2H_5)_3 + \frac{3}{2}H_2\uparrow + residue \qquad (1)$$

The AE contains the possibility of being polluted as follows:

(1) The UACs include a number of different components such as Si, Fe, Cu, Mn, Mg, Cr, Zn, Ca, Na, Ti and O except the main Al component.
(2) Various impurities including lacquer, pigment and other plastic components are coated on the surface of UACs.
(3) The AE is polluted by the high volatility of the catalyst used during the vacuum distillation.
(4) During separation, if air is infiltrated into the apparatus of vacuum distillation, the AE is converted into aluminum oxides or aluminum hydroxides as side products.

Therefore, vacuum distillation in the separation process must be accurately controlled to recover the pure AE only from the Al solu-

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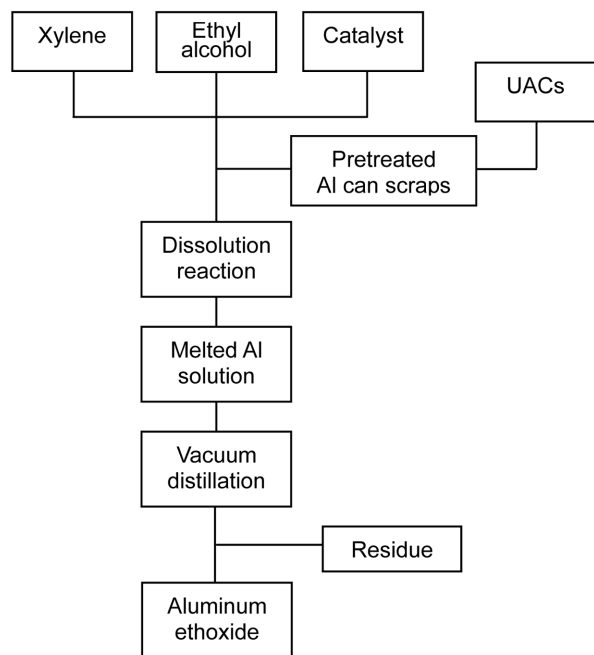E-mail: hdjang@kigam.re.kr

Fig. 1. Flowchart for synthesis of AE from UACs.

Table 1. Reaction condition for the synthesis of AE

Al (mol)	C$_2$H$_5$OH (mol)	C$_6$H$_4$(CH$_3$)$_2$ (mol)	HgI$_2$/mol Al (mol)
1	3	0.5	10^{-3}

tion after the dissolution reaction.

MATERIALS AND METHODS

UACs were cut into small pieces on a shredder, then heat-treated for 1 h at the calcination condition of 600 °C to remove the lacquer, pigment, coated plastics and other polluted materials existing in and on the UACs.

Fig. 1 presents the flowchart and Table 1 is the experimental condition for the synthesis of AE. The AE was synthesized through a dissolution reaction and vacuum distillation from pretreated Al can scraps as a reactant under the condition of 3 mol ethyl alcohol (C$_2$H$_5$OH, Daejung, >99%)/mol Al of stoichiometric ratio, adding 10^{-3} mol HgI$_2$/mol Al for catalyst (HgI$_2$, Fluka, >99.0%) and 0.5 mol xylene (C$_6$H$_4$(CH$_3$)$_2$, Daejung, >80%)/mol Al as a solvent to maintain an average of 140 °C dissolution reaction temperature [12].

After the dissolution reaction, the pure AE was separated from the melted Al solution under the condition of vacuum distillation of 200 °C and 5 mmHg.

1. Analysis

The crystal structure and crystallinity of the synthesized AE were analyzed under the following analytical conditions (CuKα Filter, scanning speed 5 °/min, 30 kV, 20 mA, 10 °≤2θ≤90 ° scanning range) on an X-ray diffraction analyzer (Rigaku).

The type and amount of bonding groups in the synthesized AE were analyzed in the range of 400-4,000 cm^{-1} wave number with a Liquid FT-infrared analyzer (FTS-60, BIO-RAD). The AE samples for the analysis were immediately dissolved in the CCl$_4$ solvent
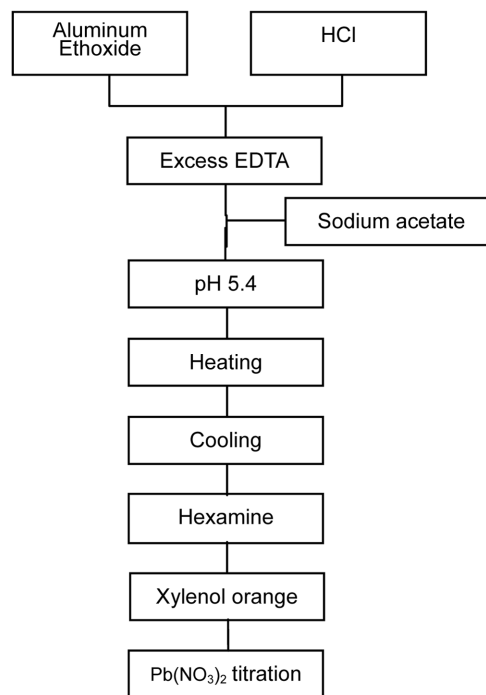

Fig. 2. Flowchart of purity analysis.

under an atmosphere of N$_2$ in glove box to prevent side reactions by water or oxygen in air after sampling.

Purity of the synthesized AE was analyzed by the complexometric method as shown in Fig. 2. First, an excess (10 ml) of EDTA (2Na) solution (Ethylenediaminetetraacetic acid disodium salt solution ([CH$_2$N(CH$_2$CO$_2$Na)CH$_2$CO$_2$H]$_2$, 0.0501 M in water, volumetric standard, Aldrich) was added to 10 ml sample solution containing 0.250 g AE per 50 ml acidic solution, and the pH was adjusted to 5.4 with buffers (acetic acid (CH$_3$COOH, ≥99.7%, Aldrich)-sodium acetate (C$_2$H$_3$O$_2$Na, min. 99.0%, Aldrich)). The sample solution was heated for a few minutes, cooled, added 1 g of hexamethylenetetraamine (C$_6$H$_{12}$N$_4$, min. 99.5%, Riedel-deHaën) and added 1 ml of 0.03% xylenol orange indicator (G.R. Daejung Chemicals & Metals Co.). The back-titration with lead nitrate solution (Pb(NO$_3$)$_2$, 0.0500 M in water, 99.99%, Aldrich) was begun. The end-point was recognizable by a very sharp color change from light-orange to pink [13].

RESULTS AND DISCUSSION

UACs were cut into small pieces on a shredder, then heat-treated for 1 h at the calcination condition of 600 °C to remove pigment, coated plastics and other polluted materials existing in the UACs as shown in Fig. 3. If the Al component is heat-treated in temperature higher than 660 °C, the Al component is dissolved and transformed into Al lump. The Al lump requires a longer dissolution reaction time because of a thick structure. Accordingly, the calcination temperature for Al can pretreatment was treated at 600 °C.

The most important process variable in the dissolution reaction is to maintain a reaction temperature of 140 °C, which is the AE melting point. In general, it is difficult to maintain the reaction temperature of 140 °C in the ethyl alcohol solvent system with the boiling
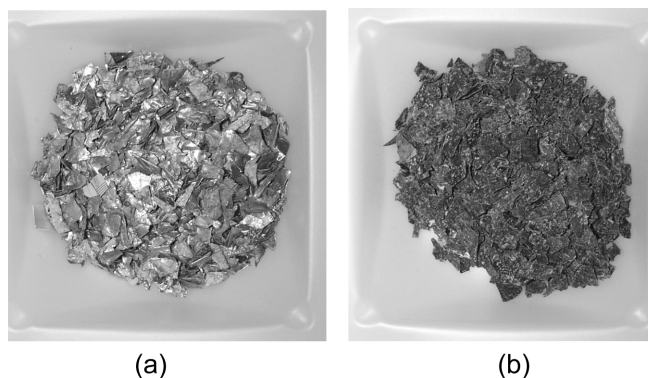
Fig. 3. Al raw materials; (a) used Al can scraps (b) pretreated Al can scraps.

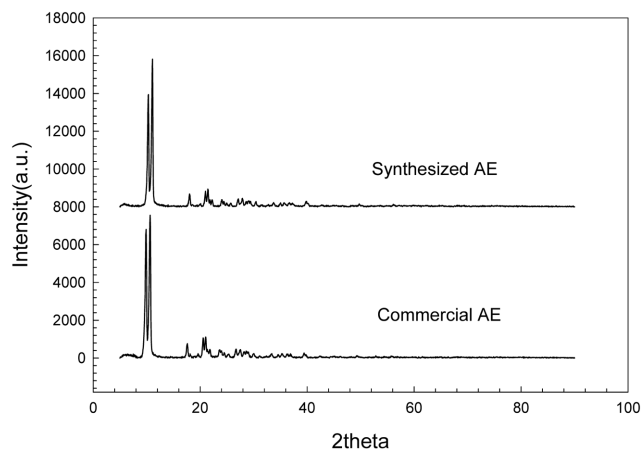
Fig. 4. XRD curves of synthesized AE and commercial AE.

Fig. 5. FT-IR curves of synthesized AE and commercial AE.

point of ethyl alcohol of 75 °C. This is because the latent heat of ethyl alcohol offsets the temperature being provided by the heating mantle to control reaction temperature. Accordingly, in this experiment, xylene in non-polar organic solvent with 140 °C boiling point was selected for the control of reaction temperature.

The role of the catalyst has not been understood completely to date, but it is known that the surface oxide layers on the UACs are softened and amalgamated by catalyst, then the Al component reacts readily with alcohol [14-19].

With the pretreated Al can scraps and ethyl alcohol as reactants, the dissolution reaction was examined at the condition of 3 mol C_2H_5OH/ mol Al of stoichiometric ratio, adding 10^{-3} mol HgI_2/mol Al for catalyst and no agitation at the reaction temperature of 140 °C. As shown in the flowchart of Fig. 1, the pretreated Al can scraps were added in the ethyl alcohol heated in advance. For the complete reaction, the dissolution reaction took about 30 h at 140 °C.

After the dissolution reaction was completed, the melted Al solution containing many impurities showed a black-colored solution phase. Therefore, in this experiment, vacuum distillation in the separation and recovery processes was carried out to separate only the pure AE only from the melted Al solution. The condition of the vacuum distillation was maintained at the range of 200 to 210 °C, 5 mmHg. At this time, the penetration of water or air into the vacuum distillation apparatus could cause the AE to produce side-products such as AlO(OH), Al(OH)₃. Therefore, the vacuum distillation reactor was designed to maintain the condition of vacuum and prevent the solidification of the AE during the process. The vacuum distillation process was carried out at the closed system to avoid the forming of aluminum hydroxide by the penetration of water or air into the apparatus. The primary phase of separated AE is colorless, transparent and molten liquid state, but the primary phase is rapidly converted to a white-solid within a few minutes. At this time, a matter that demands special attention is clogging of columns by the solidification of the AE during the vacuum distillation. Therefore, parts of the reactor including reflux column joints and recovery flask were heated by a heating coil to prevent solidification of the AE inside of the column parts during the vacuum distillation.

Fig. 4 presents the result of XRD analysis of commercial AE and the synthesized AE. The crystallinity of the synthesized AE was analyzed under the following condition (CuKα Filter, scanning speed 5 °/min, 30 kV, 20 mA, 10 °≤2θ≤90 ° scanning range) by X-ray dif-

Fig. 6. Photograph of synthesized AE and commercial AE.

fraction analyzer (Rigaku). The XRD peaks of the synthesized AE and commercial AE (Fluka Al(OC₂H₅)₃), were almost the same as

Table 2. Chemical composition of UACs

Parts	Materials	Chemical composition (%)						
		Si	Fe	Cu	Mn	Mg	Cr	Zn
Body	Al-3004	<0.30	<0.70	<0.25	1.0-1.5	0.8-1.3	-	<0.25
End	Al-5182	<0.20	<0.35	<0.15	0.2-0.5	4.0-5.0	<0.10	<0.25
Tap	Al-5082	<0.20	<0.35	<0.15	<0.15	4.0-5.0	<0.15	<0.25

the crystal structure and crystallinity as shown in Fig. 4.

Fig. 5 shows the result of the Liquid FT-infrared (FTS-60, BIO-RAD) spectra of commercial AE and our synthesized AE. The type and the amount of bonding group existing in the AE were analyzed in the range of 400 to 4,000 cm^{-1} wavelength number. In general, the characteristic absorption peak of Al-O-C bond in the AE appears at 1,059 cm^{-1} and 1,010 cm^{-1}. Vibrations arising from the Al-O$\rightarrow$ Al co-ordinate bond occur in the vicinity of 990 cm^{-1}. The 935 cm^{-1} peak is the absorption peak for the Al-O$\rightarrow$Al bond. On the other hand, the sharp peak of 800 cm^{-1} indicates the characteristic peaks of CCl_4 [2]. The absorption peaks of the synthesized AE showed that it was almost on the same level as that of the commercial AE as shown in Fig. 5.

Our study focused on the synthesis of AE with a high yield and purity in particular. Pure AE was obtained finally through vacuum distillation under the condition of 145-150 °C and 5 mmHg. After the vacuum distillation, it gave a 75% yield except the AE adhered to the inner surface of our reactor or reflux columns. This yield corresponds to the amount of total Al component existing in the UACs. Accordingly, we found that all the Al component existing in the UACs was recovered through the experimental apparatus.

The experiment must be given particular attention because the production of H_2 gas and reaction heat in the dissolution reaction has the risk of reactor explosion. If H_2O penetrates into the reactor, the AE is converted into aluminum hydroxide by hydrolysis. Accordingly, the ventilation of N_2 gas in the reactor is very important in preventing the risk of explosion by H_2 gas and reaction heat, and penetration of H_2O.

The results of purity analysis showed that our synthesized AE has a 99.1% purity as opposed to 97.8% purity of the commercial AE (Fluka, >97% purity).

Fig. 6 shows a photograph of commercial AE and our synthesized AE. In appearance, two samples were exactly the same in terms of the whiteness of powder phase.

As mentioned in the introduction, used Al can scraps include many impurities except the main Al component as shown in Table 2.

These impurities existing in the synthesized AE were analyzed by ICP (Inductively coupled plasma, GBC, Australia, Integra XL dual Mono). As the result of the analysis, various impurities described above, were not detected at all. This result shows that the synthesized AE is adequately available as a starting material for the high purity alumina.

CONCLUSIONS

This paper reports on the high purity AE synthesized in the presence of HgI_2 catalyst from UACs as a reactant through dissolution reaction and vacuum distillation.

Synthetic reaction gave a 99.1% purity. The UACs included many kinds of impurities such as Si, Fe, Cu, Mn, Mg, Cr and Zn, but the synthesized AE was found to have no impurity.

After a dissolution reaction of 30 h, the reaction gave a 75% yield. This result shows that most of the Al component existing in the UACs can was recovered through our experimental apparatus.

These findings led us to conclude that this synthetic technology of the AE from UACs may be estimated as an excellent technology in terms of high-value added applications and environmental protection regulations that exclude Al dross formation in the conventional Al can recycling processing.

ACKNOWLEDGMENT

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