Preparation of Aluminumtriethoxide by Application of Aluminum Corrosion

Osami Seri and Daichi Sasaki*

Muroran Institute of Technology, Faculty of Engineering, Muroran 050-8585, Japan

Aluminumtriethoxide were obtained when aluminum powder was refluxed in dehydrated ethanol containing aluminum chloride for 10 ks. It is shown that aluminumtriethoxide powder made in our laboratory coincided with that supplied in commercial market by similar pattern of XRD-analysis, particle size distribution analysis and particle morphology observation. It is considered that aluminumtriethoxide in our laboratory was electrochemically interpreted as corrosion product which has been oxidized in ethanol containing aluminum chloride as catalyst.

Keywords: aluminum triethoxide, corrosion product, electrochemical, chloride ions, oxidation-reduction reaction

1. Introduction

It is well known that aluminum oxide (alumina) is one of the most important materials for industrial fields, such as furnace-construction materials, abrasives and catalyst carriers. Also the alumina is widely used in our dairy life, due to its superiorities not only in heat-resistance, corrosion resistance, and electric insulation, but also medical harmlessness. There are many preparation processes for alumina such as Bayer process, heat decomposition of alum and sol-gel method.1) Among them, it is well known that sol-gel method is a relatively new method for alumina preparation. It is pointed out that the preparation of alkoxide for sol-gel method has some merits and demerits.2) The merits are followings: it is possible ① to synthesize at low temperature, ② to obtain homogeneity in microscopic order, ③ to synthesize various oxides with new compositions, ④ to prepare a ceramics to gain good efficiency in production process. The demerits are followings: it may occur that ① organic matters are sometimes left in product, ② composition of alkoxide may be changed to other compounds during sintering process, ③ shrinkages in size and change of shape may happen during sintering, and ④ generally too expensive.

As an example 3) of aluminum alkoxides aluminum propoxide has been obtained as following processes. Roughly speaking, its process has three steps: step1 is that metallic aluminum powder and isopropanol are mixed together and then refluxed in a reaction tower. Step2 is that the mixed slurry obtained in step1 are heated and kept until the slurry will change into aluminum isopropoxide. Step3 is that the alkoxide in step2 is distilled into pure alkoxide and dried to solid powder in a vacuum atmosphere. In the above process the aluminumisopropoxide is prepared by heating an isopropanol environment with addition of mercury chloride. It is often said that any of aluminum alkoxide now in use will be expensive for utilization in industrial fields.2) Because aluminum alkoxides have some faults such as complicated process in removing environmental poison such as mercury and low efficiency in manufacturing.

From the electrochemical point of view, both of the preparation of aluminum alkoxide and corrosion phenomena of aluminum must be interpreted as same oxidation-reduction reaction of electrochemical process. The only difference between them is their environments, the former is alcohol and the latter is water. The above interpretation leads to an idea that electrochemical analysis and its consideration used in corrosion phenomena in water environment can be applied to the preparation for aluminum alkoxide.

In order to obtain the electrochemical possibility for low-cost preparation of aluminum alkoxide, dissolution behavior of aluminum in an alcohol environment has been electrochemically investigated. Trial and error experiments guides to new findings that aluminum alkoxide (aluminum triethoxide) has been synthesized in an ethanol with an addition of aluminum chloride. We report a fundamental technology for aluminum alkoxide production in low-cost and simple handlings.4)

2. Experiments

2.1 Ingredients

Aluminum powder (Kanto Chemical Co. Ltd, 99.99 mass%, Al), aluminumtriethoxide (Kanto Chemical Co. Ltd, 95.0 mass%, Al(OC₂H₅)₃), anhydrous aluminum chloride (Kanto Chemical Co. Ltd, 98.0 mass%, AlCl₃), dehydrated ethanol (Kanto Chemical Co. Ltd, 99.5 volume%, C₂H₅OH) and de-ionized water were used.

2.2 Preparation of aluminumalkoxide (aluminumtriethoxide)

Metallic aluminum powder (3 g) and AlCl₃ (30 g) were mixed, and then completely blended by using a magnetic mixing mortar for 1.8 ks. The powder above was immediately mixed and then poured into a flask with 300 ml volume which has contained 200 ml ethanol. The flask was refluxed by a mantle heater for about 10 ks. It has been confirmed that gas evolved in the refluxing process was hydrogen gas by a gas chromatograph analysis. After the refluxing process, grey-colored solution was obtained. The solution was heated again to be solid state in an electric-heating apparatus at the temperature of 351 K. For the purpose of following inspections and analyses, the solid state substance was crushed and re-grinded by the magnetic mixing mortar.
2.3 Measurements

The aluminum alkoxide obtained by our method was identified by using XRD analysis, particle size distribution analysis and particle morphology observation. For this purposes, a desktop X-ray diffraction apparatus (Rigaku Co. Ltd, MiniflexII), automatic particle measurement apparatus (Nikkisou Co. Ltd, MT3000) and transmission electron microscope (JOEL Co. Ltd, JEM-2000FX) were used.

3. Results

3.1 XRD analysis

Ten kinds of powders, which are aluminum alkoxide powders made in our laboratory and aluminumtriethoxide powders supplied as a commercial product, were calcinated at various temperature (298 K of room temperature, 573 K, 873 K, 1173 K and 1473 K) by electric furnace for about 3.6 ks and then XRD-analyzed.

Figure 1(a) shows XRD-analysis results of our laboratory powders and Fig. 1(b) shows commercial powders. The X-ray profile patterns at temperatures of 298 K, 573 K and 873 K in Fig. 1(a) show typical amorphous structures of aluminum hydroxide, because their profiles indicate gentle and gradual flat pattern but not crystallographic peak patterns. The curve at 1173 K has two peaks at the scattering angle of around $2\theta = 46^\circ$ and $2\theta = 67^\circ$ which may be crystal structure $\gamma$-alumina. It was found that X-ray profile curve at 1473 K completely coincided with that of $\alpha$-alumina. Comparing curves in Fig. 1(a) to that in Fig. 1(b), it is clear that X-ray curves of our alkoxide powder calcinated at 573, 873, 1173 and 1473 K show complete agreement with that of the aluminum triethoxide in market, except for low range at 298 K.

3.2 Particle size distribution

We compared the particle size distributions between our aluminum alkoxide powder and the aluminum triethoxide powder in market. After the powder (3 g) was poured into beaker with 100 ml ethanol, the beaker was strongly shaken for about 600 s by ultrasonic apparatus and then measured its particle size distribution by the automatic particle measurement apparatus. Figure 2(a) and Fig. 2(b) show typical examples of our powder and commercial powder, respectively. Figure 2(a) shows that frequency curve may be roughly divided into three areas: area $\ominus$ submicron ($0.2\sim1 \mu m$) distribution, area $\circ$ several micron ($1\sim10 \mu m$) distribution and area $\oplus$ several dozens micron ($30\sim80 \mu m$) distribution. The accumulation curve of area $\ominus$ and area $\circ$ in Fig. 1(a) tells us that almost all of powders were in size of submicron order. The characteristics of the area $\oplus$ exhibit shape with gentle and gradual slope distribution, but not the well-known normal distribution. The differences between Fig. 2(a) and Fig. 2(b) lie on two experimental facts; there are disappearance of the area $\ominus$ of Fig. 1(a), and whole shape of the distributions in Fig. 2(b) is shifted to right direction side from that of the Fig. 2(a).
3.3 Particle morphology

The particle shape of aluminum alkoxide powder in our laboratory and the aluminumtriethoxide in market were observed by TEM. Figure 3(a) and Fig. 3(b) show each typical examples.

Left-hand side photo in Fig. 3(a), which is our aluminum alkoxide powder, shows various size particles; submicron and several micron size particles are scattered. Right-hand side photo in Fig. 3(a), which is detailed photo, is composed with gathering of some $0.2-0.5\mu m$ size particles by observing the shadows of the particles. In Fig. 3(b) which is aluminumtriethoxide powder in market, it is often confirmed that larger size particles are also constructed by gatherings of some smaller size (submicron size) particles.

4. Discussion

4.1 Synthesis of metal alkoxide

It is well-known that the sol-gel method is one of the most important methods to prepare materials for ceramics, glasses, catalysis, etc. and the metal alkoxide is important precursor material for the method. Roughly summarizing, there are two ways to obtain alkoxide materials: one is by oxidation-reduction reaction and another is by substitution reaction. Two ways for the alkoxide reactions above are generally expressed as followings.

$$M + nROH \rightarrow M(OR)_n + nH_2 \uparrow \quad (1)$$
$$MCl_n + nROH \rightarrow M(OR)_n + nHCl \quad (2)$$

where, M is metal elements, R is alkyl group.

The oxidation-reduction reaction expressed in eq. (1) will proceed in quantitative manner, but unfortunately oxidation-reduction reaction of eq. (1) is restricted to a few metals such as lithium and sodium. The substitution reaction of eq. (2) will proceed in poor reaction efficiency, since very few chloride ions of metal chloride $MCl_n$ can be substituted with alkyl function (-OR) and also long reaction time is needed.
4.2 Aluminum hydroxide and aluminum alkoxide as corrosion product

The well-known reaction of aluminum corrosion in water is expressed as a following reaction.

\[ \text{Al} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3/2\text{H}_2 \uparrow \quad (3) \]

The aluminum hydroxide Al(OH)_3, and hydrogen gas H_2, as corrosion product will be obtained. Aluminum in an alcohol environment will be corroded as the following chemical reaction and then an aluminum alkoxide and hydrogen gas H_2 will be obtained as corrosion product. When an alcohol is ethanol, corrosion product will be aluminumtriethoxide Al(OEt)_3.

\[ \text{Al} + 3\text{Et-}\text{OH} = \text{Al(OEt)}_3 + 3/2\text{H}_2 \uparrow \quad (4) \]

Equation above will be divided into two reactions; anodic and cathodic reactions as followings,

\[
\begin{align*}
\text{Al} & \to \text{Al}^{3+} + 3e \\
3\text{Et-}\text{OH} + 3e & \to 3\text{Et-O}^- + 3/2\text{H}_2 \uparrow
\end{align*}
\]

(5)

(6)

It is well known for corrosion scientists and engineers that the corrosion rate of eq. (3) will be accelerated when the water environment was contaminated with chloride ions.\(^7\) It is electrochemically recognized that anodic new reaction between aluminum and chloride ions will be formed when an environment contains chloride ions. For example, a following anodic reaction will occur as an new anodic reaction.

\[ \text{Al} + 3\text{Cl}^- \to \text{AlCl}_3 + 3e \quad (7) \]

Same anodic reaction of the eq. (7) will occur even if an environment is an alcohol which contains chloride ions. The anodic reaction above must be rapid reaction, so-called “fast system”,\(^8\) because it has experimentally been found that the eq. (7) has been severely attack reaction for aluminum. The eqs. (5), (6) and (7) will simultaneously and vigorously occur when an environment will be heated. Since the relationship between eq. (5) and eq. (7) is characterized as mutual and competitive reactions. A reaction which shows more rapid reaction rate will determine dominant rate of whole anodic reaction. The relation between electrode potential and current density (eqs. (5), (6) and (7)), which is expressed as respective partial polarization curve, are followings,\(^8,11\)

\[
\begin{align*}
E = E_{\text{Al/Al}^{3+}}^{90} + \frac{RT}{3F} \ln \frac{1}{k_{\text{Al}^{3+}}} + \frac{RT}{3F} \ln i_a + i_a \cdot \rho_{\text{AlO}_3} \cdot l \\
E_{\text{Et-O}^-/\text{Et-}OH}^{90} + \frac{RT}{2F} \ln k_{\text{Et-O}^-} \cdot k_{\text{H}} - \frac{3RT}{2F} \ln (-i_c) \quad (8) \\
E_{\text{Al/AlCl}_3}^{90} + \frac{RT}{F} \ln k_{\text{Cl}^-} - \frac{RT}{F} \ln \left(\frac{1}{k_{\text{Cl}^-} - i_a}\right) \quad (9) \\
E_{\text{Al/AI}^{3+}}^{90}, E_{\text{Et-O}^-/\text{Et-}OH}^{90} \quad \text{and} \quad E_{\text{Al/AlCl}_3}^{90} \quad \text{is standard formal electrode potential: V vs.SHE,} \quad F \quad \text{is Faraday constant:} \quad 96.5 \times 10^3 \text{C} \cdot \text{mol}^{-1}, \quad R \quad \text{is gas constant:} \quad 8.31 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \quad T \quad \text{is absolute temperature: K,} \quad k_{\text{Al}^{3+}}, k_{\text{Et-O}^-}, k_{\text{H}}, \quad \text{and} \quad k_{\text{Cl}^-} \quad \text{are the coefficients regarding diffusion of} \quad \text{Al}^{3+} \text{ion,} \quad \text{Et-O}^- \text{ion,} \quad \text{hydroxide gas and} \quad \text{Cl}^- \text{ion in ethanol:} \quad \text{A} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}, \quad \rho_{\text{AlO}_3} \quad \text{is the specific resistance of aluminum oxide:} \quad \text{k} \Omega \cdot \text{cm,} \quad l \quad \text{is thickness of} \quad \text{Al}_2\text{O}_3 \text{oxide film: cm,} \quad k_{\text{Cl}^-} \quad \text{is diffusion limit current density of chloride ion: mA} \cdot \text{cm}^{-2}. \quad (9,12) \\
\end{align*}
\]

Hence, the polarization curves in eqs. (5), (6) and (7) will be plotted by substituting numerical values, which are tabulated in Table 1, for items in eqs. (8), (9) and (10).

\[
\text{Table 1} \quad \text{Estimated values of chemical thermodynamic properties in Fig. 4.}
\]

<table>
<thead>
<tr>
<th>Formula</th>
<th>rate</th>
<th>( \Delta G^\circ / \text{kJ} \cdot \text{mol}^{-1} )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>cr</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>aq</td>
<td>-485</td>
<td>-478</td>
</tr>
<tr>
<td>Et-\text{OH}</td>
<td>1</td>
<td>-175</td>
<td>-156</td>
</tr>
<tr>
<td>Et-\text{O}^-</td>
<td>aq</td>
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<td>-95</td>
</tr>
<tr>
<td>H_2</td>
<td>g</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cl^-</td>
<td>aq</td>
<td>-131</td>
<td>-125</td>
</tr>
<tr>
<td>AlCl_3</td>
<td>cr</td>
<td>-692</td>
<td>-617</td>
</tr>
</tbody>
</table>

Fig. 4 Schematic explanation of corrosion of aluminum in an ethanol environment.

4.3 Characteristics of aluminumtriethoxide made in our laboratory

Aluminumtriethoxide is used in various industrial fields such as catalyst of polymerization reactions, transmaterial for esterification reactions, cross-linker substances for paints and material of ceramics or medicines.\(^13\) In Japan only one company is recorded as the aluminumtriethoxide manufacturers,\(^13\) but detailed information about the aluminumtriethoxide production is not opened. The main reasons why the only one company supplies the aluminumtriethoxide may
be have some disadvantages such as complicated production process, long times for hydrolysis, safety and easy handling problems and so on.

The merits and demerits of our aluminumtriethoxide production may be as follows:

(Merits)
1. It is possible to prepare by simple equipments.
2. It is possible to make the aluminumtriethoxide easy; at low temperature (usually under about 373 K) and in a short time (less than a few hours).
3. It is possible to quantitatively evaluate the production process and estimate quantity of the aluminumtriethoxide by assistance of corrosion science and engineering knowledge.

(Demerits)
1. It is necessary that a corrosion-resistant material will be needed for plant and equipment materials due to the chloride ion.
2. It will be necessary to have a closed system process due to the evolution and spread of organic gases such as ethyl chloride and diethyl ether.

It is difficult to evaluate the advantage/disadvantage between our aluminum triethoxide method and commercial method in details, because the present preparation methods in the market are absolutely unclear. But it will be expected that cost will be lower by our method, because our merit (1) and (2) are more superior ways to have cost-cutting process. And our method will have more advantageous in environmentally harmless process such as mercury-free process and various production routes when quantitative analysis of merit (3) will be carried out in careful manner.

5. Conclusion

When metallic aluminum powder were poured into dehydrated ethanol with AlCl₃ and then refluxed for about 3 h, aluminumtriethoxide were obtained. Aluminumtriethoxide powder made in our laboratory and that supplied in commercial market showed almost same results of XRD analysis, particle size distribution and particle morphology observation. In the corrosion science and technology point of view, it was considered that the aluminumtriethoxide obtained above is interpreted as aluminum corrosion product corroded in ethanol. It is possible to analyze corrosion reaction of aluminum in ethanol: the electrochemical procedure for corrosion reaction of aluminum in water can apply to the preparation of aluminumtriethoxide in ethanol.

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REFERENCES