The Separation of Aluminium Trichloride and Iron Trichloride by Selective Hydrogen Reduction

Yuichi SHOJI, Ryoko MATSUZAKI, and Yuzo SAEKI*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 227

(Received March 12, 1981)

Synopsis. When a gaseous mixture generated by heating a mixture of $AlCl_3$ and $FeCl_3$ (<19 wt%) was introduced, with a hydrogen stream, into a reaction zone held at various temperatures, the iron content in the sublimate decreased markedly above 300 °C; $AlCl_3$ containing less than 10 ppm of iron was obtained at 600 °C.

The production of aluminium *via* the electrolysis of aluminium trichloride($AlCl_3$) or the production of special-grade alumina from $AlCl_3$ requires pure $AlCl_3$. The $AlCl_3$ produced by the chlorination of aluminium-containing materials, however, contains impurities, such as iron, silicon, and titanium chlorides.

The separation of silicon tetrachloride or titanium tetrachloride from $AlCl_3$ presents no special problems because of the sufficient difference in relative volatility and the absence of vapor-phase complexes. The removal of iron trichloride($FeCl_3$) from $AlCl_3$ has been described as being considerably difficult despite the high volatility of pure $AlCl_3$ relative to the pure $FeCl_3$ phase,[1,2] because of the formation of a volatile complex, $AlFeCl_6$, on heating a mixture of $AlCl_3$ and $FeCl_3$.[1,3]

Considering the relative ease of the reduction of Fe(III) to Fe(II), the present authors examined the separation of $FeCl_3$ from $AlCl_3$ by means of selective hydrogen reduction.

Experimental

The $AlCl_3$ used was prepared by the reaction between aluminium (Al: 99.99%) and chlorine at 400 °C.[4] The $FeCl_3$ used was prepared by the reaction between iron (Fe: 99.98%) and chlorine at 500 °C.[5] The hydrogen used was purified up to a dew point below −70 °C by passing it through a membrane of palladium heated at 400 °C.

To examine the $FeCl_3$ content in the sublimate on heating a mixture of $AlCl_3$ and $FeCl_3$ in an argon stream, a mixture of $AlCl_3$ and $FeCl_3$ at a specified ratio in a quartz boat (width: 16 mm, length: 72 mm, depth: 9 mm) was placed in a straight, transparent quartz tube (inner diameter: 24 mm, length: 1000 mm) and heated at 150 °C for 1 h in the middle of a tubular electric furnace (heating length: 300 mm) in an argon stream at a flow-rate of 150 cm³/min. The temperature of the sample part was controlled within ±2 °C.

For the experiments on the separation of $FeCl_3$ from $AlCl_3$ by means of selective hydrogen reduction, a gaseous mixture generated by heating a mixture of $AlCl_3$ and $FeCl_3$ at 150 °C was introduced, with a hydrogen stream at a flow-rate of 150 cm³/min, into a reaction zone (inner diameter: 24 mm, length: 280 mm) held at a specified temperature for 1 h.

The total amount of aluminium and iron in the sublimate obtained outside the reaction zone was determined by chelatometric titration,[6] while the amount of iron was determined colorimetrically as 1, 10-phenanthroline complex[7] by using a Shimadzu double-beam spectrophotometer, Model UV-200S. The amount of aluminium was determined by subtracting the amount of iron from the above total amount of aluminium and iron. The chlorine content was determined gravimetrically as AgCl.

Throughout this work, chlorides of aluminium and iron were handled in an argon atmosphere to prevent any contamination by moisture in the air.

Results and Discussion

The $FeCl_3$ content in the sublimate obtained by heating 5.0 g of a mixture of $AlCl_3$ and $FeCl_3$ at a specified ratio in an argon stream was examined. Considering the vapor pressures of $AlCl_3$ and $FeCl_3$, the heating temperature was maintained at 150 °C ($P_{Al_2Cl_6}=11.53\times10^3$ Pa, $P_{Fe_2Cl_6}=1.4$ Pa).[8] The results are shown in Fig. 1.

Jorgensen and Moyle[9] have examined the equilibrium in the $AlCl_3$–$FeCl_3$–Cl_2 system and described that the vapor pressures of Al_2Cl_6, $AlFeCl_6$, and Fe_2Cl_6 at 160—180 °C are not changed by the initial $FeCl_3$ content in the range of 5—50 mol% (6—55 wt%). From the above description, we could well understood that the $FeCl_3$ content in the sublimate was constant on heating a mixture of $AlCl_3$ and $FeCl_3$ with an initial $FeCl_3$ content above 3 wt%. The results shown in Fig. 1 indicate that the clean separation of $FeCl_3$ from $AlCl_3$ is difficult by a repetition of the fractional sublimation.

Next, experiments for separating $FeCl_3$ from $AlCl_3$ by selective hydrogen reduction were carried out. The $FeCl_3$ content in the sublimate obtained by heating 5.0 g of a mixture of $AlCl_3$ and $FeCl_3$ at a specified ratio in a hydrogen stream at 150 °C was examined. The results obtained were the same as those obtained by the heating in an argon stream, shown in Fig. 1.

Then, the gaseous mixture generated by heating 5.0 g of a mixture of 95 wt% $AlCl_3$ and 5 wt% $FeCl_3$ at 150 °C (Fe content in the gaseous mixture: 1.4_6 wt% as $FeCl_3$ or 0.5_0 wt% as Fe) was introduced,

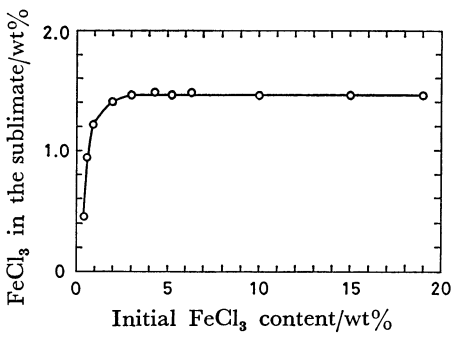

Fig. 1. $FeCl_3$ contents in the sublimates obtained by heating mixtures of $AlCl_3$ and $FeCl_3$ at various ratios in an argon stream.

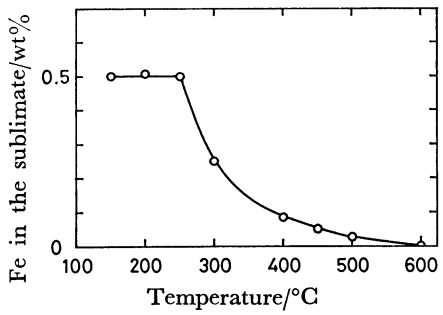

Fig. 2. Fe contents in the sublimates obtained by heating the gaseous mixture, generated by heating a mixture of $AlCl_3$ and $FeCl_3$, in a hydrogen stream at various temperatures.

with a hydrogen stream at a flow-rate of 150 cm^3/min, into a reaction zone held at various temperatures for 1 h. The iron content in the sublimate obtained outside the reaction zone was then examined. The results are shown in Fig. 2.

When the temperature of the reaction zone was below 250 °C, no change in the iron content was observed. Above 300 °C, the iron content decreased markedly, being reduced to 0.002 wt% at 600 °C. At 300—450 °C, it was observed that a colorless powder was deposited in the reaction zone. This colorless powder was identified as iron dichloride($FeCl_2$) by chemical analysis. Above 500 °C, the formation of iron in the form of thin film was observed in addition to $FeCl_2$.

The vapor pressure of $FeCl_2$ is negligible in the temperature range of this experiment.[8] However, it could also be considered that a part of the $FeCl_2$ formed was carried by the hydrogen stream and contaminated the sublimate. Therefore, the sublimate obtained above 400 °C was heated in an argon stream at 150 °C, and the iron content in the sublimate obtained outside the heating zone was examined. From the results, the iron contents were found to be 0.006 wt% at 400 °C, 0.004 wt% at 450 °C, 0.003 wt% at 500 °C, and <0.001 wt% at 600 °C.

From these experimental results, it is revealed that $AlCl_3$ containing less than 10 ppm of iron can be obtained by introducing a gaseous mixture, generated by heating a mixture of $AlCl_3$ and $FeCl_3$, with a hydrogen stream into a reaction zone held at 600 °C.

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