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Synthesis of β-ZrClN by Thermal Decomposition of Zirconium(IV) Amide Trichloride

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Synopsis. The zirconium amide trichloride $ZrCl_3(NH_2)\cdot 7NH_3$ was prepared by the reaction of $ZrCl_4$ with liquid ammonia. On heating up to 600 °C in flowing ammonia gas, the amide was efficiently converted into β-ZrClN, whereas under vacuum it was decomposed to a different product. The decomposition processes were followed by using a quartz spring balance.

In a preceding study, we showed that a layer structured crystal β-ZrClN could be a promising candidate for electrochromic electrode, since the crystal forms a lithium intercalation compound, and exhibits reversible color changes between pale yellow green and black.[1,2]

The powder sample of β-ZrClN for the study was prepared according to a similar procedure reported by Juza and Heners:[3] Anhydrous zirconium tetrachloride was subjected to react with a dry ammonia in a silica glass tube installed horizontally in an electric furnace. The disadvantage of this procedure is that the yield of β-ZrClN is as low as 20—30%. The low yield is mainly due to the formation of the additional compound of ammonia $ZrCl_4\cdot 2NH_3$ which is easily vaporized above 400 °C[4] and physically transported to the cooler parts outside the heating zone before being decomposed to β-ZrClN.

In the present study, a new preparation method has been developed by thermal decomposition of the zirconium(IV) amide trichloride $ZrCl_3(NH_2)\cdot 7NH_3$ in an ammonia stream.

Experimental

Preparation of Zirconium Amide Chloride. Drake and Fowles[5] revealed that $ZrCl_4$ was subjected to ammonolysis to only one Zr–Cl bond in liquid ammonia, giving the zirconium amide chloride:

$$ZrCl_4 + (n+2)NH_3 \longrightarrow ZrCl_3(NH_2)\cdot nNH_3 + NH_4Cl$$

They removed the resulting ammonium chloride by washing the separated solid with liquid ammonia repeatedly. In this study, a glass apparatus was used, which was so designed that the ammonium chloride could be continuously leached out with liquid ammonia, as shown in Fig. 1. The apparatus works essentially as a Soxhlet extraction unit. Under a dry nitrogen atmosphere, about 4 g of zirconium tetrachloride purified by sublimation was placed on the glass filter E in the reaction tube D, the upper end of which is connected to a Dry Ice–methanol condenser B by a ground joint. Dry ammonia gas (99.999%) was introduced into the apparatus through the valve A and liquefied by the condenser. The liquefied ammonia comes down and reacts with the $ZrCl_4$ on the glass filter. The ammonium chloride formed by the reaction was dissolved in the liquid ammonia and leached out into the flask F connected below by a ground joint. The ammonia gas rising from the flask through the bypass C can also be liquefied by the condenser. After refluxing for 3 h, the liquid ammonia was removed and the apparatus was purged with dry nitrogen. The amide was left on the glass filter in the form of white flocculent.

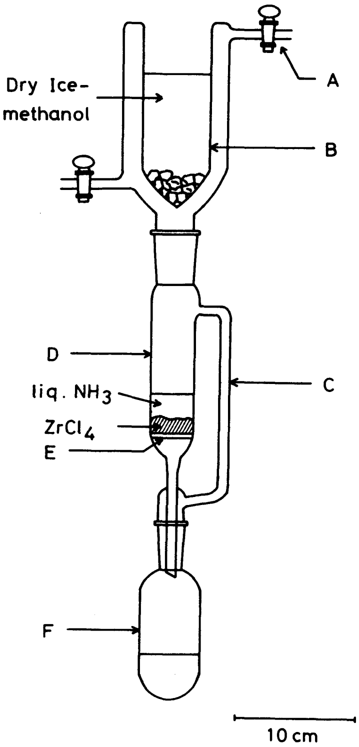

Fig. 1. Soxhlet type glass apparatus used for the preparation of zirconium amide trichloride.

Analyses. A weighed amount of the reaction product was dissolved in 2 mol dm^{-3} sulfuric acid, and the zirconium content was determined gravimetrically as ZrO_2 after precipitation with sodium hydroxide. Nitrogen and chlorine contents were analyzed on the sulfuric acid solution by Kjeldahl and Fajans' methods, respectively.

The thermogravimetric analysis of the zirconium amide chloride was carried out by using a quartz spring balance in a vacuum and in an ammonia stream for a heating rate of 3 °C min^{-1}. The flow rate of the ammonia was 50 ml min^{-1}.

Results and Discussion

The chemical analysis of the product showed that the contents of Zr, N, and Cl were 28.1, 33.6, and 31.5%, respectively. This analytical result corresponds to the atomic ratio Zr:N:Cl=1.00:7.8:2.9, indicating that only one of the Zr–Cl bonds was subjected to ammonolysis and that the zirconium amide chloride with an approximately stoichiometric composition $ZrCl_3(NH_2)\cdot 7NH_3$ was obtained.

The thermogravimetric analysis (TG) curves of the zirconium amide chloride are shown in Fig. 2. On evacuation at room temperature for 3 h, the amide

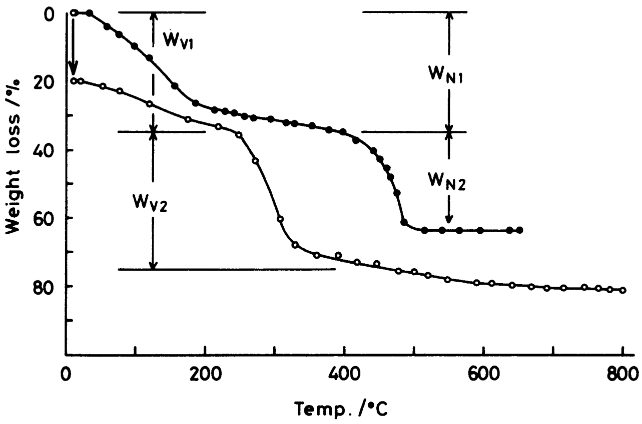

Fig. 2. Thermogravimetric curves for zirconium amide trichloride $ZrCl_3(NH_2)\cdot 7NH_3$ measured in a vacuum (○) and in an ammonia stream (●).

lost about 4 moles of ammonia, and then 3 moles of ammonia are gradually removed up to 240 °C.

$$ZrCl_3(NH_2)\cdot 7NH_3 \longrightarrow ZrCl_3(NH_2)\cdot 3NH_3 + 4NH_3$$

$$ZrCl_3(NH_2)\cdot 3NH_3 \longrightarrow ZrCl_3(NH_2) + 3NH_3$$

In the second decomposition stage accompanied by a steep weight loss beginning from 280 °C, white sublimate consisting of $ZrCl_4$ and NH_4Cl appeared on the cooler parts of the glass walls. Probably, the following decomposition occurs in this heating stage:

$$2ZrCl_3(NH_2) \longrightarrow ZrClN + ZrCl_4 + NH_4Cl$$

The amount of the weight loss for this reaction was calculated to be 67%. On the ammoniate formula ($ZrCl_3(NH_2)\cdot 7NH_3$) basis, this amount is reduced to 43%, which is in good agreement with the amount of the loss W_{V2} (40%). Yellow solid having the atomic ratio $Zr_{1.0}Cl_{1.0}N_{0.8}$ was obtained when the decomposition was interrupted at 450 °C. The solid was very reactive and took fire when dropped into water. Irrespective of the similarity of the atomic ratio, it is apparent that the solid is different from our desired β-ZrClN which is stable in water. Similar unkown yellow solid was also found by Fowles and Pollard[6] in the course of the preliminary study of the decomposition of the zirconium amide trichloride. On further heating up to 800 °C, the sample lost the weight gradually and gave black powder, which was found to be ZrN by X-ray powder diffraction analysis.

Even in an ammonia stream, the amount of the first weight loss (W_{N1}) corresponded almost to the first weight loss (W_{V1}) observed in a vacuum. However, the second weight loss began at the temperature higher by about 150 °C than that of the decomposition in a vacuum. The residue obtained after the decomposition at 650 °C was identified to be β-ZrClN by X-ray powder diffraction analysis. The amount of the weight loss (ammoniate formula basis) calculated on the basis of the following reaction was 22%:

$$ZrCl_3(NH_2) + 2NH_3 \longrightarrow ZrClN + 2NH_4Cl$$

Although the amount of the weight loss W_{N2} (29%) was a little larger than the calculated amount, it is apparent that the zirconium amide trichloride could be effficiently converted into β-ZrClN. It should be noted that in the ammonia stream, the decomposition temperature of $ZrCl_3(NH_2)$ is much higher than the temperature in a vacuum. It seems likely that the ammonia suppresses the decomposition of the amide, and that no sooner the $ZrCl_4$ is evolved at the higher decomposition temperature than it reacts with ammonia, forming β-ZrClN.

The resulting β-ZrClN formed lithium intercalation compound and showed changes in color from pale yellow green to black by soaking into butyl lithium solution in hexane.

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