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The Preparation of Vanadium Tetrachloride from Vanadium Dichloride Oxide and Vanadium Trichloride and the Hydrogen Reduction Process of Vanadium Tetrachloride

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The reactions of VCl_2O and VCl_3 with chlorine, and the reaction of VCl_3O, formed by the chlorination of VCl_2O, with chlorine in the presence of carbon were examined. The products formed by the reaction between gaseous VCl_4 and hydrogen at various temperatures, and the behavior of VCl_3 and VCl_2 on heating in a hydrogen stream were examined. The reaction between VCl_2O and chlorine occurs above *ca.* 120 °C and proceeds markedly above *ca.* 170 °C to form VCl_3O. VCl_4 can be obtained by passing the gaseous VCl_3O together with chlorine through a carbon bed held at *ca.* 700 °C. The reaction between VCl_3 and chlorine occurs above *ca.* 80 °C and proceeds markedly above *ca.* 170 °C to form VCl_4. The hydrogen reduction process of VCl_4 in the vapor phase may be represented as follows: The reaction between VCl_4 and hydrogen, $2VCl_4(g)+H_2(g)\rightarrow 2VCl_3(s)+2HCl(g)$, proceeds above *ca.* 500 °C to form VCl_3. Subsequently, the hydrogen reduction of the VCl_3, $2VCl_3(s)+H_2(g)\rightarrow 2VCl_2(s)+2HCl(g)$, and the disproportionation of the VCl_3, $2VCl_3(s)\rightarrow VCl_2(s)+VCl_4(g)$, proceed to form VCl_2. Above *ca.* 620 °C, the reaction between the VCl_2 and hydrogen, $VCl_2(s)+H_2(g)\rightarrow V(s)+2HCl(g)$, proceeds to form vanadium.

The vanadium trichloride oxide (VCl_3O) which is dissolved in the titanium tetrachloride ($TiCl_4$) prepared by the chlorination of titanium ores is commercially removed as a non-volatile vanadium-containing precipitate by bubbling hydrogen sulfide through the $TiCl_4$. The present authors[1] have previously reported that the precipitate formed by the reaction between VCl_3O and hydrogen sulfide is a mixture of vanadium dichloride oxide (VCl_2O), vanadium trichloride (VCl_3), and sulfur. The sulfur can be selectively separated by heating the mixture at *ca.* 250 °C in an argon stream.[2,3]

From the view point of resources utilization, it is important to obtain fundamental information on the preparation of vanadium tetrachloride (VCl_4) from the mixture of VCl_2O and VCl_3 and on the preparation of vanadium by the hydrogen reduction of the VCl_4.

There has been no report on the reaction between VCl_2O and chlorine. It has been reported that VCl_3 reacts with chlorine at 600 °C to form VCl_4.[4] Regarding the hydrogen reduction of VCl_4 in the vapor phase, Jantsch and Zemek[5] have reported that vanadium is obtained by the hydrogen reduction of VCl_4 at 680—700 °C. On the other hand, it has been reported that vanadium dichloride (VCl_2) is obtained by the reaction between VCl_4 and hydrogen above 650 °C,[6] or at 750—800 °C.[7]

In this paper, the reactions of VCl_2O and VCl_3 with chlorine, and the reaction of VCl_3O, formed by the chlorination of VCl_2O, with chlorine in the presence of carbon were examined. The hydrogen reduction process of VCl_4 in the vapor phase was also examined.

Experimental

Materials. The VCl_2O used was prepared from VCl_3, divanadium trioxide(V_2O_3), and VCl_3O,[8] and confirmed to be VCl_2O[9] by X-ray analysis. The chemical analysis gave V, 37.0; Cl, 51.4% (Calcd for VCl_2O: V, 36.96; Cl, 51.44%). VCl_3 was obtained by the thermal decomposition of VCl_4 at 180 °C in an argon atmosphere,[3] and confirmed to be VCl_3[10] by X-ray analysis. The chemical analysis gave V, 32.4; Cl, 67.6% (Calcd for VCl_3: V, 32.38; Cl, 67.62%). VCl_3O was prepared by the reaction between V_2O_5, which had been obtained by the thermal decomposition of guaranteed reagent ammonium metavanadate, and chlorine in the presence of carbon at 300 °C.[11] The chemical annlysis gave V, 29.4; Cl, 61.3% (Calcd for VCl_3O: V, 29.40; Cl, 61.37%). Carbon was obtained by the thermal decomposition of guaranteed reagent glucose. VCl_4 was prepared by the reaction between vanadium (V, 99.8% up) and chlorine at 500 °C.[3] The chemical analysis gave V, 26.4; Cl, 73.5% (Calcd for VCl_4: V, 26.43; Cl, 73.57%). VCl_2 was obtained by the disproportionation of VCl_3 in an argon stream at 650 °C,[3] and confirmed to be VCl_2[12] by X-ray analysis. The chemical analysis gave V, 41.8; Cl, 58.1% (Calcd for VCl_2: V, 41.81; Cl, 58.19%).

Experimental Procedures. The percentages of reacted VCl_2O or VCl_3 on heating in a chlorine stream at various temperatures for a specified period were examined as follows: The sample (1.0 g) in a quartz boat (60 mm length, 13 mm width, 7 mm depth) was placed in a straight reaction tube (17 mm i. d.) with a condenser. Chlorine was introduced into the reaction tube at a flow-rate of 50 cm^3/min. The sample part was then placed in the center of an electric furnace (300 mm in heating length) maintained at a specified temperature. The weight loss of the sample on heating in a chlorine stream for a specified period was measured. The temperature of the sample part was controlled to within ±2 °C.

The reaction between VCl_3O and chlorine in the presence of carbon was examined as follows: Gaseous VCl_3O was formed by heating VCl_3O (27 g) at 120 °C and carried by a stream of argon (40 cm^3/min) to a carbon bed (30 mm diameter, 150 mm length) held at a specified temperature. Chlorine was simultaneously introduced at a flow-rate of 100 cm^3/min through a separate tube into the carbon bed. The mean flow-rate of gaseous VCl_3O was 10.7 cm^3/min. The reaction was allowed to proceed for 1 h.

The products obtained by the hydrogen reduction of VCl_4 in the vapor phase at various temperatures were examined as follows: Gaseous VCl_4 was formed by heating VCl_4 (28 g) at 130 °C and carried by a stream of argon (50 cm^3/min) to the reaction zone (28 mm i. d., 250 mm length) held at a specified temperature. Hydrogen was simultaneously introduced at a flow-rate of 150 cm^3/min through a separate tube into the reaction zone. The mean flow-rate of gaseous VCl_4 was 7.4

cm^3/min. A quartz or high purity alumina tube was inserted inside the reaction tube. The reaction was allowed to proceed for 2 h.

Throughout this work, the chlorides and chloride oxides of vanadium were handled in an argon atmosphere or *in vacuo* to prevent any contamination from moisture in the air.

Thermogravimetry (TG). The sensitivity of the quartz helix used for TG was approximately 67 mm/g. The sample (0.15 g) was heated at a rate of 2.5 °C/min and the flow-rate of chlorine or hydrogen was maintained at 50 cm^3/min.

Analytical. X-Ray analysis of the solid sample was performed using Ni filtered Cu radiation. The sample chamber of the diffractometer was maintained under dry nitrogen atmosphere to prevent the contamination of the sample from moisture in the air during the irradiation.

The vanadium content in the sample was determined by chelatometric titration;[13] the chlorine content was gravimetrically determined as AgCl, after dissolving the sample in dilute nitric acid.

Results and Discussion

Preparation of Vanadium Tetrachloride from Vanadium Dichloride Oxide and Vanadium Trichloride. *Reaction between VCl_2O and Chlorine*: On heating VCl_2O in an argon stream, the VCl_2O disproportionates above *ca.* 295 °C according to the reaction, $2VCl_2O(s) \rightarrow VClO(s) + VCl_3O(g)$, as previously reported by the present authors.[2] The TG curve of VCl_2O in a chlorine stream showed that VCl_2O began to react with chlorine before disproportionating and that the weight loss reached 100%. The percentages of reacted VCl_2O on heating VCl_2O in a chlorine stream at various temperatures for 0.25—3 h were examined. At 110 °C, no reaction product was observed. The results obtained at various temperatures above 120 °C are shown in Fig. 1.

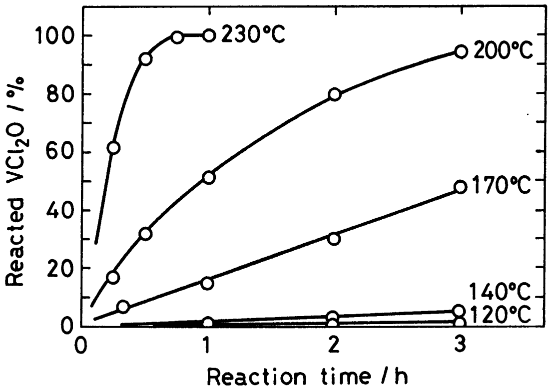

Fig. 1. Effect of temperature on the reaction between VCl_2O and chlorine.

The chemical analysis of the reaction product obtained by heating VCl_2O at 200 °C in a chlorine stream gave V, 29.4; Cl, 61.3%. From this result, the reaction product between VCl_2O and chlorine was found to be VCl_3O (Calcd: V, 29.40; Cl, 61.37%).

The above-mentioned results reveal that VCl_2O reacts with chlorine above *ca.* 120 °C according to the reaction,

$$2VCl_2O(s) + Cl_2(g) \longrightarrow 2VCl_3O(g), \qquad (1)$$

and the reaction proceeds markedly above *ca.* 170 °C.

Since the vapor pressure of VCl_3O is 12.3 mmHg[8] even at room temperature (20 °C), the VCl_3O formed by heating VCl_2O (5.0 g) in a chlorine stream (100 cm^3/min) at 200 °C for 2 h was condensed in a trap held at 20 °C, 0 °C (P_{VCl_3O}=4.0 mmHg),[8] or −18 °C (P_{VCl_3O}=1.2 mmHg).[8] The percentage of the amount of VCl_3O condensed in the trap held at 20 or 0 °C to the calculated value based on the amount of reacted VCl_2O was 82 or 94%, respectively. When the temperature of the cooling trap was −18 °C, it was observed that a small amount of chlorine was dissolved in the condensed VCl_3O.[14] The amount of chlorine dissolved in the VCl_3O was determined as follows: after the chlorination was over, the VCl_3O was allowed to warm up to 0 °C in an argon atmosphere in order to liberate the chlorine from the VCl_3O. The liberated chlorine was absorbed in sodium hydroxide (NaOH) solution. A small amount of VCl_3O which vaporized during the above procedure was also absorbed in the NaOH solution. The total amount of chlorine in the NaOH solution was gravimetrically determined as AgCl, while the vanadium content in the NaOH solution was also determined by chelatometric titration. From the vanadium content, the amount of the VCl_3O absorbed in the NaOH solution was calculated. The amount of chlorine dissolved in the VCl_3O was calculated by subtracting the amount of chlorine corresponding to the VCl_3O absorbed in the NaOH solution from the total amount of chlorine in the NaOH solution. The result showed that the VCl_3O condensed in the trap held at −18 °C contained 2.0% of chlorine. The percentage of the amount of VCl_3O obtained after liberating the chlorine to the calculated value based on the amount of reacted VCl_2O was 97%.

Reaction between VCl_3 and Chlorine: On heating VCl_3 in an argon stream, the VCl_3 disproportionates above *ca.* 350 °C according to the reaction, $2VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$, as previously reported by the present authors.[3] The TG curve of VCl_3 in a chlorine stream showed that VCl_3 began to react with chlorine before disproportionating and that the weight loss reached 100%. The percentages of reacted VCl_3 on heating VCl_3 in a chlorine stream at various temperatures for

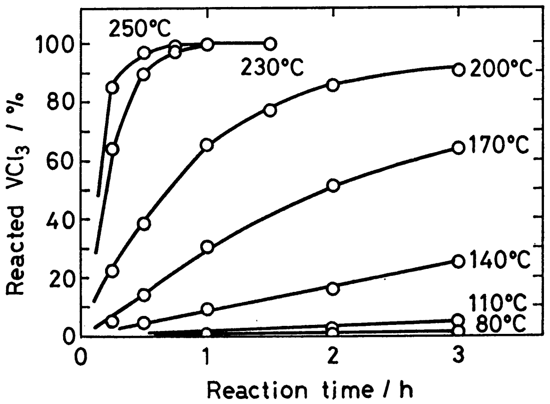

Fig. 2. Effect of temperature on the reaction between VCl_3 and chlorine.

0.25—3 h were examined. At 70 °C, no reaction product was observed. The results obtained at various temperatures above 80 °C are shown in Fig. 2.

The chemical analysis of the reaction product obtained by heating VCl_3 in a chlorine stream at 200 °C gave V, 26.4; Cl, 73.5%. From the result, the reaction product between VCl_3 and chlorine was found to be VCl_4 (Calcd: V, 26.43; Cl, 73.57%).

The above-mentioned results reveal that VCl_3 reacts with chlorine above *ca.* 80 °C according to the reaction,

$$2VCl_3(s) + Cl_2(g) \longrightarrow 2VCl_4(g), \qquad (2)$$

and that the reaction proceeds markedly above *ca.* 170 °C.

Since the vapor pressure of VCl_4 is 5.4 mmHg[15] even at room temperature (20 °C), the VCl_4 formed by heating VCl_3 (5.0 g) in a chlorine stream (100 cm^3/min) at 200 °C for 2 h was condensed in a trap held at 20 °C, 0 °C ($P_{VCl_4}=1.7$ mmHg),[15] or −18 °C ($P_{VCl_4}=0.5$ mmHg).[15] The percentage of the amount of VCl_4 condensed in the trap held at 20 °C to the calculated value based on the amount of reacted VCl_3 was 92%. When the temperature of the cooling trap was 0 or −18 °C, it was observed that a small amount of chlorine was dissolved in the condensed VCl_4.[16] The VCl_4 formed is allowed to warm up to 20 °C in an argon atmosphere in order to liberate the chlorine. The amount of chlorine dissolved in the VCl_4 was determined in the same manner as described in the experiment on VCl_2O. From the results, the amounts of chlorine dissolved in the VCl_4 condensed at −18 and 0 °C were 0.7 and 4.0%, respectively. The percentage of the amount of VCl_4 obtained after liberating the chlorine to the calculated value based on the amount of reacted VCl_3 was 96% at 0 °C and 97% at −18 °C.

Reaction between VCl_3O and Chlorine in the Presence of Carbon: As mentioned above, VCl_3O is formed by the reaction between VCl_2O and chlorine. To obtain knowledge of formation of VCl_4 from the VCl_3O, the products obtained by passing gaseous VCl_3O together with chlorine through a carbon bed held at various temperatures were examined. The results are shown in Table 1.

TABLE 1. REACTION PRODUCT BETWEEN GASEOUS VCl_3O AND CHLORINE IN THE PRESENCE OF CARBON

Temp / °C	Chemical analysis/% V	Chemical analysis/% Cl	Product/% VCl_4	Product/% VCl_3O
400	29.4	61.3	—	100
500	28.7	64.3	24	76
600	27.3	70.0	71	29
650	26.7	72.5	91	9
700	26.4	73.5	100	—

The chloride and chloride oxide of vanadium in the liquid state at room temperature are VCl_4 (Calcd: V, 26.43; Cl, 73.57%) and VCl_3O (Calcd: V, 29.40; Cl, 61.37%). This fact and the chemical analysis shown in Table 1 showed that VCl_4 was formed above 500 °C, and that the weight percentage of VCl_4 increased with increasing temperature. At 700 °C, VCl_4 alone was obtained. When VCl_4 formed by the chlorination of VCl_3O at 700 °C in the above manner was condensed in a trap cooled at −18 °C, VCl_4 was obtained in a 97% yield.

The above-mentioned results suggest that the following method is preferable for preparing VCl_4 from a mixture of VCl_2O and VCl_3: By heating a mixture of VCl_2O and VCl_3 at *ca.* 200 °C in a chlorine stream, VCl_4 and VCl_3O are formed. Subsequently, VCl_4 is prepared by passing the gaseous mixture of VCl_4 and VCl_3O together with chlorine through a carbon bed held at *ca.* 700 °C. The resulting VCl_4 is condensed in a trap cooled at −18 °C.

Hydrogen Reduction Process of Vanadium Tetrachloride. Reduction Products of Gaseous VCl_4 with Hydrogen: Prior to the examination of the hydrogen reduction of VCl_4 in the vapor phase, the thermal decomposition of gaseous VCl_4 was examined to know whether the thermal decomposition of gaseous VCl_4 occurs under the experimental conditions of this work. The experimental procedure was the same as that for the hydrogen reduction described in the previous paragraph, except that argon was introduced into the reaction zone instead of hydrogen at the same flow-rate as that of hydrogen.

The experimental results showed that 0.009 g of VCl_3 and 0.002 g of chlorine were formed by the thermal decomposition of gaseous VCl_4 at 200, 600, and 1000 °C, regardless of the heating temperature. The result indicated that *ca.* 0.1% of gaseous VCl_4 introduced into the reaction zone thermally decomposed. From the result, it was considered that the decomposition of gaseous VCl_4 could be neglected in the discussion about the experimental results for the hydrogen reduction of gaseous VCl_4, to be described later.

The products formed by heating gaseous VCl_4 in a hydrogen stream at various temperatures were examined by X-ray analysis and chemical analysis. At 400 °C, it was observed that the reaction between gaseous VCl_4 and hydrogen did not proceed. The results obtained above 500 °C are shown in Table 2.

TABLE 2. REDUCTION PRODUCTS OF GASEOUS VCl_4 WITH HYDROGEN AT VARIOUS TEMPERATURES

Temp / °C	Products and their yields/mol% In the reaction zone V	VCl_2	VCl_3	Outside the reaction zone V	VCl_2	VCl_3	Unreacted VCl_4/mol%
500	—	<1	2	—	—	1	96
600	—	23	—	—	19	<1	56
700	2	63	—	—	34	—	—
800	4	64	—	<1	31	—	—
900	34	29	—	6	30	—	—
1000	76	—	—	23	—	—	—

The results indicate that the reaction between gaseous VCl_4 and hydrogen proceeds above *ca.* 500 °C, giving VCl_3 and VCl_2 at 500—600 °C, VCl_2 and vanadium at 700—900 °C, and vanadium alone at 1000 °C.

Behavior of VCl_3 and VCl_2 on Heating in a Hydrogen Stream: In order to reveal the hydrogen reduction process of gaseous VCl_4, the behavior of VCl_3 and VCl_2, formed during the reduction process, on heating in a hydrogen stream was examined.

The TG curve of VCl_3 in a hydrogen stream is shown in Fig. 3(a). The result showed that VCl_3 began to react with hydrogen at *ca.* 270 °C before the disproportionation described in the previous paragraph occurred. The sample heated up to 600 °C was found to be VCl_2 by X-ray analysis. The formations of hydrogen chloride and VCl_4 were observed during the weight loss. The final weight loss was 47.7%. This value was larger than the calculated value, 22.54%, based on the hydrogen reduction of VCl_3 to form VCl_2,

$$2VCl_3(s) + H_2(g) \longrightarrow 2VCl_2(s) + 2HCl(g), \qquad (3)$$

and was smaller than the calculated value, 61.27%, based on the disproportionation of VCl_3 to form VCl_2,

$$2VCl_3(s) \longrightarrow VCl_2(s) + VCl_4(g). \qquad (4)$$

These facts were considered to indicate that, on heating VCl_3 in a hydrogen stream, both the hydrogen reduction and the disproportionation of VCl_3 occurred. The experimental value of the weight loss showed that 35% of VCl_3 was reduced with hydrogen and 65% of VCl_3 disproportionated.

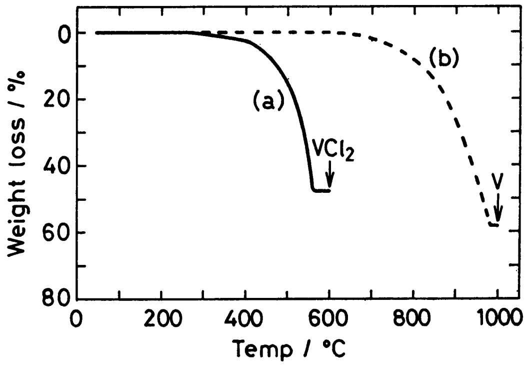

Fig. 3. TG curves of VCl_3 and VCl_2 in a hydrogen stream.
(a): VCl_3, (b): VCl_2.

From the results, on heating VCl_3 in a hydrogen stream, the hydrogen reduction of VCl_3 (Reaction 3) occurs above *ca.* 270 °C, and the disproportionation of VCl_3 (Reaction 4) occurs above *ca.* 350 °C in addition to Reaction 3. This result is contrary to the result by Pechkovskii and Vorob'ev,[17] who reported that on heating VCl_3 in a hydrogen stream above *ca.* 480 °C, VCl_2 was formed by the hydrogen reduction of VCl_3.

The TG curve of VCl_2 in a hydrogen stream is shown in Fig. 3(b). In this case, a platinum basket was used for TG, because it had been reported that vanadium reacted with quartz above *ca.* 1000 °C.[18] The sample heated up to 1000 °C was found to be vanadium[19] by X-ray analysis.

These results reveal that on heating VCl_2 in a hydrogen stream, VCl_2 reacts with hydrogen to form vanadium above *ca.* 620 °C according to the reaction,

$$VCl_2(s) + H_2(g) \longrightarrow V(s) + 2HCl(g). \qquad (5)$$

Consideration on Hydrogen Reduction Process of VCl_4: From the above-mentioned results, the hydrogen reduction process of VCl_4 in the vapor phase was discussed.

As shown in Table 2, on heating VCl_4 in a hydrogen stream, VCl_3 and VCl_2 were formed at 500—600 °C. The only reaction which gave VCl_3 was thought to be

$$2VCl_4(g) + H_2(g) \longrightarrow 2VCl_3(s) + 2HCl(g), \qquad (6)$$

since the thermal decomposition of gaseous VCl_4 scarcely proceeded as described before. The reactions which gave VCl_2 were considered to be the hydrogen reduction and the disproportionation of the VCl_3, since the hydrogen reduction of VCl_3 (Reaction 3) occurs above *ca.* 270 °C and the reduction is accompanied by the disproportionation (Reaction 4) above *ca.* 350 °C, as described before. As shown in Table 2, above 700 °C, vanadium was formed in addition to VCl_2, and vanadium alone was obtained at 1000 °C. Since VCl_2 is reduced with hydrogen to vanadium (Reaction 5) above *ca.* 620 °C, it was considered that the vanadium obtained was formed by the hydrogen reduction of the VCl_2 formed by Reactions 3 and 4.

These results allow us to represent the hydrogen reduction process of VCl_4 in the vapor phase as follows: the reaction between gaseous VCl_4 and hydrogen proceeds above *ca.* 500 °C to form VCl_3 (Reaction 6). Subsequently, the hydrogen reduction of the VCl_3 (Reaction 3) and the disproportionation of the VCl_3 (Reaction 4) proceed to form VCl_2. Above *ca.* 620 °C, the reaction between the VCl_2 and hydrogen proceeds to form vanadium (Reaction 5).

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