Reaction Processes of Vanadium Dichloride Oxide and Vanadium Trichloride with Oxygen

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The products formed by the heating of VCl_2O in an oxygen stream at various temperatures were examined by chemical and X-ray analysis. The reaction products between VCl_3 and oxygen were examined in the same manner. The reaction process between VCl_2O and oxygen may be represented as follows: VCl_2O reacts with oxygen above *ca.* 170 °C to form V_2O_5 and VCl_3O, $12VCl_2O(s)+3O_2(g)\rightarrow 2V_2O_5(s)+8VCl_3O(g)$, and this reaction is accompanied by the reaction, $4VCl_2O(s)+3O_2(g)\rightarrow 2V_2O_5(s)+4Cl_2(g)$. The reaction process between VCl_3 and oxygen may be represented as follows: VCl_3 reacts with oxygen above *ca.* 100 °C to form VCl_3O, $2VCl_3(s)+O_2(g)\rightarrow 2VCl_3O(g)$, and this reaction is accompanied by the reaction, $2VCl_3(s)+O_2(g)\rightarrow 2VCl_2O(s)+Cl_2(g)$.

Vanadium trichloride oxide (VCl_3O) which is dissolved in crude 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 crude $TiCl_4$. The present authors[1)] have previously reported that the vanadium-containing precipitate formed by the reaction between VCl_3O and hydrogen sulfide is a mixture of vanadium dichloride oxide (VCl_2O) and a small amount of vanadium trichloride (VCl_3). From the view point of waste reclamation, it is necessary to understand the chemical process for the preparation of divanadium pentaoxide (V_2O_5) and chlorine by the oxidation of the mixture of VCl_2O and VCl_3 with oxygen (air).

There has been no report on the reaction process between VCl_2O and oxygen. Regarding the reaction between VCl_3 and oxygen, Ruff and Lickfett[2)] have reported that VCl_3O is formed by heating VCl_3 at *ca.* 500—600 °C in an oxygen stream. Lamprey and Forsyth[3)] have briefly described that the reaction, $VCl_3+1/2O_2\rightarrow VCl_3O$, mainly occurs above 250 °C on heating VCl_3 in air. Pechkovskii and Vorob'ev[4)] have reported that the reaction between VCl_3 and oxygen to form VCl_3O mainly occurs above 200 °C on heating VCl_3 in an oxygen stream, and that onyl a small part of the VCl_3 is oxidized to V_2O_5.

In this paper, the reaction processes of VCl_2O and VCl_3 with oxygen will be revealed.

Experimental

The VCl_2O used was prepared from VCl_3, divanadium trioxide (V_2O_3), and VCl_3O by the method based on the literature.[5)] Chemical analysis of the VCl_2O obtained gave V, 37.0; Cl, 51.4% (Calcd for VCl_2O: V, 36.96; Cl, 51.44 %); it was confirmed to be VCl_2O[6)] by X-ray analysis. VCl_3 was obtained by the thermal decomposition of VCl_4, which was prepared by the reaction between vanadium (V, 99.8% up) and chlorine at 500 °C,[7)] at 180 °C in an argon atmosphere.[8)] The chemical analysis gave V, 32.4; Cl, 67.6% (Calcd for VCl_3: V, 32.38; Cl, 67.62%); it was confirmed to be VCl_3[9)] by X-ray analysis. The oxygen was dried by passing it through conc. sulfuric acid and over diphosphorous pentaoxide.

The sensitivity of the quartz helix used for thermogravimetry (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 argon or oxygen was maintained at 50 cm^3/min.

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 with moisture in air during the irradiation.

The products obtained by heating VCl_2O and VCl_3 in an oxygen stream at various temperatures were examined by the following procedures: 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 (16 mm i. d.) with a water-cooled condenser. Oxygen was introduced into the reaction tube at a flow-rate of 50 cm^3/min. The sample part was then placed in the centre of an electric furnace (300 mm in heating length) maintained at a specified temperature for a specified period. The temperature of the sample part was controlled to within ±2 °C.

The liquid product (VCl_3O) was collected in a trap cooled in solid carbon dioxide through the condenser. The chlorine formed was absorbed in KI solution through the trap and determined by iodometry. The total amount of chlorine formed during the reaction was determined by adding the above value and the amount of chlorine dissolved in the liquid product in the solid carbon dioxide trap.[10)] The determination of the amount of chlorine dissolved in the liquid product will be described later.

Chemical analysis of the solid and liquid products was performed as follows: The vanadium content in the sample was determined by chelatometric titration,[11)] while the chlorine content was gravimetrically determined as AgCl, after dissolving the sample in dilute nitric acid.

The amount of chlorine dissolved in the liquid product in the solid carbon dioxide trap was determined as follows: After the reaction was over, the liquid product was allowed to warm to room temperature in an argon atmosphere in order to liberate the chlorine from the liquid product. The liberated chlorine was absorbed in NaOH solution. A small amount of the liquid product 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 and the vanadium content in the NaOH solution was also determined by chelatometric titration. From the vanadium content, the amount of the liquid product absorbed in the NaOH solution was calculated. The amount of chlorine dissolved in the liquid product was calculated by subtracting the amount of chlorine corresponding to the liquid product absorbed in the NaOH solution from the total amount of chlorine in the NaOH solution.

The total amount of liquid product formed was corrected by adding the amount of liquid product absorbed in the NaOH solution to the amount of liquid product in the trap.

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

Results and Discussion

Reaction Process between Vanadium Dichloride Oxide and Oxygen. It has been reported that on heating VCl_2O in an inert atmosphere, the disproportionation occurs above 300 °C[12] or 330 °C,[4] according to the reaction, $2VCl_2O(s) \rightarrow VClO(s) + VCl_3O(g)$.

Prior to the examination of the reaction between VCl_2O and oxygen, the behavior of VCl_2O on heating in an argon stream was examined. The TG curve showed that VCl_2O lost weight continuously above *ca.* 295 °C and the weight reached a constant value at *ca.* 380 °C. The sample heated up to 380 °C was shown to be VClO[13] by X-ray analysis. The weight loss at 380 °C was 62.9%. This value was in good agreement with the calculated value, 62.86%, based on the disproportionation of VCl_2O. The gaseous product was confirmed to be VCl_3O by chemical analysis of the product obtained by heating VCl_2O (1.0 g) in an argon stream at 370 °C for 3 h. From these results, it is confirmed that VCl_2O disproportionates above *ca.* 295 °C according to the reaction, $2VCl_2O(s) \rightarrow VClO(s) + VCl_3O(g)$.

The TG curve of VCl_2O in an oxygen stream showed that VCl_2O reacted appreciably with oxygen above *ca.* 180 °C before disproportionating. To obtain more detailed information on the reaction between VCl_2O and oxygen, the products formed by heating VCl_2O at various temperatures for 0.5—3 h in an oxygen stream were examined by X-ray and chemical analysis.

At 160 °C, no reaction product was observed. The reaction products obtained at various temperatures above 170 °C and their weight percentages to the initial VCl_2O were determined by chemical and X-ray analysis.[6,14,15] The results are summarized in Table 1.

The most stable oxide phase of vanadium under the conditions of this work is V_2O_5.[16] Trivanadium heptaoxide (V_3O_7) was not formed below 240 °C as shown in Table 1, but a small amount of V_3O_7 was formed in addition to V_2O_5 above 260 °C. As shown in Table 1, the reaction between VCl_2O and oxygen proceeded markedly above 260 °C to form a large amount of gaseous VCl_3O. Consequently, the reaction between VCl_2O and oxygen has been thought to proceed under a low oxygen concentration to form V_3O_7 in addition to V_2O_5. The solid products obtained by heating VCl_2O (1.0 g) at 290 °C under various flow-rates of oxygen for 1 h were examined. The results are shown in Table 2.

TABLE 2. SOLID PRODUCTS BETWEEN VCl_2O AND OXYGEN AT VARIOUS FLOW-RATES OF OXYGEN

O_2 flow-rate/ $cm^3\ min^{-1}$	Solid product/%		Unreacted VCl_2O/%
	V_2O_5	V_3O_7	
50	66	3	31
100	71	1	28
200	73	—	27

From the results, it was observed that V_3O_7 was not formed under a high flow-rate of oxygen. This confirms the above consideration on the formation of V_3O_7.

The experimental results for the reaction products between VCl_2O and oxygen at various temperatures, shown in Table 1, indicated that V_2O_5 and VCl_3O were the main products. This fact was considered to indicate that the main reaction on heating VCl_2O in an oxygen stream was the reaction,

$$12VCl_2O(s) + 3O_2(g) \longrightarrow 2V_2O_5(s) + 8VCl_3O(g). \quad (1)$$

TABLE 1. REACTION PRODUCTS BETWEEN VCl_2O AND OXYGEN AT VARIOUS TEMPERATURES

Temp/°C	Reaction time/h	Product/%				Unreacted VCl_2O/%
		In the boat		Outside the heating zone		
		V_2O_5	V_3O_7	VCl_3O	Cl_2	
170	3	<1	—	0.4	<0.1	>99
200	3	1	—	2.8	<0.1	96
220	3	7	—	21.6	0.9	72
240	0.5	4	—	12.6	0.5	83
	1	7	—	23.6	0.8	69
	3	15	—	48.9	1.7	38
260	0.5	8	<1	26.3	0.9	66
	1	14	<1	46.0	1.6	41
	3	22	1	75.7	2.6	3
280	0.5	10	<1	33.7	1.1	57
	1	19	<1	63.4	2.3	19
	3	23	<1	77.6	2.7	<1
290	0.5	15	<1	50.5	1.8	35
	1	21	1	70.8	2.5	10
	2	23	1	78.4	2.8	0

TABLE 3. REACTION PRODUCTS BETWEEN VCl_3 AND OXYGEN AT VARIOUS TEMPERATURES

Temp/°C	Reaction time/h	Product/%			Unreacted VCl_3/%
		In the boat	Outside the heating zone		
		VCl_2O	VCl_3O	Cl_2	
100	6	<1	6.8	<0.1	93
110	6	<1	14.3	0.2	86
130	3	<1	19.4	0.2	81
	6	1	37.5	0.3	64
150	1	<1	17.2	0.1	83
	3	1	43.8	0.3	58
	6	2	75.7	0.5	29
160	1	<1	31.0	0.2	70
	3	2	87.4	0.6	17
	6	3	105.2	0.8	0

The possible reactions giving the chlorine (in Table 1) were considered to be the reaction,

$$4VCl_2O(s) + 3O_2(g) \longrightarrow 2V_2O_5(s) + 4Cl_2(g), \qquad (2)$$

and the reaction between gaseous VCl_3O formed by Reaction 1 and oxygen,

$$4VCl_3O(g) + 3O_2(g) \longrightarrow 2V_2O_5(s) + 6Cl_2(g). \qquad (3)$$

As reported in the previous report,[17] Reaction 3 does not proceed below 400 °C. Consequently, the formation of a small amount of chlorine obtained by heating VCl_2O in an oxygen stream was considered to be due to Reaction 2.

Based on this assumption, the amount of V_2O_5 formed by Reaction 2 was calculated from the amount of chlorine formed (in Table 1). The molar ratio of the amount of VCl_3O to the amount of V_2O_5 obtained by subtracting the amount of V_2O_5 formed by Reaction 2 from the total amount of V_2O_5 formed was calculated to be approximately 4: 1. In this calculation, the amount of V_3O_7 formed was converted into that of V_2O_5 on the assumption that V_3O_7 was oxidized to V_2O_5. These results confirmed that the main reaction which occurred by heating VCl_2O in an oxygen stream was Reaction 1 and that this reaction was accompanied by Reaction 2.

The above-mentioned results reveal that VCl_2O reacts with oxygen above *ca.* 170 °C according to Reaction 1 and that this reaction is accompanied by Reaction 2. As a result, V_2O_5 (under a low oxygen concentration, V_3O_7 is formed in addition to V_2O_5), VCl_3O, and a small amount of chlorine are formed.

Reaction Process between Vanadium Trichloride and Oxygen. 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.[17]

The TG curve showed that VCl_3 reacted appreciably with oxygen above *ca.* 110 °C before disproportionating. To obtain more detailed information on the reaction between VCl_3 and oxygen, the products formed by heating VCl_3 at various temperatures for 1—6 h in an oxygen stream were examined.

At 90 °C, no reaction product was observed. The reaction products obtained at various temperatures above 100 °C and their weight percentages to the initial VCl_3 were determined by chemical and X-ray analysis.[6,9] The results are summarized in Table 3.

The experimental results shown in Table 3 indicated that VCl_3O was the main product by the reaction between VCl_3 and oxygen. This fact was considered to indicate that the main reaction on heating VCl_3 in an oxygen stream was the reaction,

$$2VCl_3(s) + O_2(g) \longrightarrow 2VCl_3O(g). \qquad (4)$$

Small amounts of VCl_2O and chlorine were formed in addition to VCl_3O. The molar ratio of the amount of VCl_2O to the amount of chlorine was calculated to be approximately 2: 1. This fact was considered to indicate that the reaction,

$$2VCl_3(s) + O_2(g) \longrightarrow 2VCl_2O(s) + Cl_2(g), \qquad (5)$$

occurred in addition to Reaction 4.

Based on the assumption that the formation of VCl_2O and chlorine was due to Reaction 5, the amount of VCl_3 consumed by Reaction 5 was calculated from the amount of chlorine formed (in Table 3). The molar ratio of the amount of VCl_3O formed to the amount of the reacted VCl_3 obtained by subtracting the amount of VCl_3 consumed by Reaction 5 from the total amount of the reacted VCl_3 was calculated to be approximately 1: 1. These results confirmed that the main reaction which occurred by heating VCl_3 in an oxygen stream was Reaction 4 and that this reaction was accompanied by Reaction 5.

The above-mentioned results reveal that VCl_3 reacts with oxygen above *ca.* 100 °C according to Reaction 4 and that this reaction is accompanied by Reaction 5. As a result, VCl_3O and small amounts of VCl_2O and chlorine are formed.

As mentioned above, Pechkovskii and Vorob'ev[4] have reported that on heating VCl_3 in an oxygen stream, a small part of the VCl_3 is oxidized to V_2O_5. From the results of this work, it is probable that the V_2O_5 is formed by the reaction of VCl_2O, formed by Reaction 5, with oxygen.

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