Chemistry

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON THE PROCESS AND PRODUCTS OF THE HYDROLYTIC DECOMPOSITION OF TITANIUM TETRACHLORIDE

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The least studied is the vapor-phase hydrolysis of titanium tetrachloride at relatively low temperatures (25–150°), when the formation is possible not of dioxide, but of titanium oxy- and hydroxychlorides (^1). The latter may form as by-products in processes of chlorination of titanium-containing raw materials (^2,3) and rectification of technical titanium tetrachloride (^4). Information on the conditions of formation and the properties of titanium oxy- and hydroxychlorides is scant and often contradictory (^4-6).

In the present work we studied the interaction of $TiCl_4$ vapor with H_2O vapor in a dynamic system in the temperature range 25–750°. The ratio of the molar concentrations of $TiCl_4$ and H_2O in the reaction mixture was 1 : 1, 1 : 2, 1 : 3, and 1 : 4, respectively. The experimental part of the study consisted in saturating an inert carrier gas, with respect to the reagents, with definite amounts of $TiCl_4$ and H_2O vapors, after which the two streams were combined at a specified temperature in the reactor; the reaction products were trapped and subjected to further study. In all experiments the interaction of $TiCl_4$ with H_2O vapor began immediately after their contact in the reactor, which was visually observed from the formation of a white smoke (aerosol), whereas Hudson (^1) reports that the indicated reaction occurs only several minutes after mixing the reagents. It was established that changing the mean residence time of the reagent mixture in the reaction zone from 11.85 sec to 0.23 sec (a decrease by ~50 times) has no substantial influence on the magnitude of the degree of hydrolytic decomposition of $TiCl_4$. Evidently, the vapor-phase hydrolysis of $TiCl_4$ proceeds with extremely high speed.

Fig. 1. Dependence of the titanium content in $TiCl_4$ hydrolysis products on the reaction temperature:
A –1 : 1; *B* –1 : 2; *V* –1 : 3; *G* –1 : 4

Figure 2

Figure 2: Figure 2

Particles of the solid reaction products obtained in the temperature range 25-150° are very fine, but have the property of sticking together with the formation of small, shapeless, highly hygroscopic lumps; therefore all work with them was carried out in a chamber filled with dry air. They have a yellowish coloration, the intensity of which decreases with increasing hydrolysis temperature and with increasing molar concentration of water in the reaction mixture. It was established that these substances are good dielectrics.

The composition of the $TiCl_4$ hydrolysis products, as shown by Figs. 1 and 2, depends on the conditions under which they are obtained. Changing the $TiCl_4$: H_2O ratio in the reaction mixture from 1 : 1 to 1 : 3 leads to a decrease in the titanium content and

chlorine in the hydrolysis products (curves A, B, V). However, at the ratio $TiCl_4 : H_2O = 1 : 4$, the titanium content increases and the chlorine content decreases (curve G in Figs. 1 and 2) in the hydrolysis products obtained at temperatures of 25, 50, and 75°. The latter phenomenon is associated with the interaction of the $TiCl_4$ hydrolysis products with vapors of "excess" water, leading to the liberation of HCl from the indicated substances.

The composition of the vapor-phase hydrolysis products of $TiCl_4$, obtained in the temperature range 25-150° and consisting of compounds of variable composition, is proposed to be expressed by the formulas:

$$TiO_a(OH)_{2-2a}Cl_2, \qquad \text{where } a = 0 \div 1;$$

$$Ti(OH)_{xCl_{(4-x)}} \cdot nH_2O, \qquad \text{where } x : (4-x) = 1 \div 3.$$

Thus, the results of experiments on the hydrolytic decomposition of $TiCl_4$ in the temperature range 25-150° showed that the actual reaction cannot be expressed by any of the simple equations usually cited in the literature ([5,6]). Complete hydrolytic decomposition of $TiCl_4$ did not occur in the experiments described even at 300°, since the reaction product obtained at this temperature contained about 15% chloride ion, rather strongly bound to titanium. At 500° the product of $TiCl_4$ hydrolysis was TiO_2, containing no more than 2% chloride ion. At 750° the chloride-ion content in TiO_2 decreases to 0.1-0.2%.

Fig. 2. Dependence of the chlorine content in the $TiCl_4$ hydrolysis products on the reaction temperature. Designations as in Fig. 1

Fig. 3 presents a typical picture of the dependence of the change in weight of $TiCl_4$ hydrolysis products, obtained in the range 25-100°, on the time of their

Figure 3

Figure 3: Figure 3

residence in atmospheric air. As is seen from Fig. 3, the curve of weight change at first rises sharply, reaching a maximum, after which a decrease in weight occurs. This is explained by the fact that, along with adsorption of moisture by the $TiCl_4$ hydrolysis product, a chemical reaction occurs between it and the added water, with liberation of hydrogen chloride into the gas phase. After a certain time, the rate of water adsorption by the substance becomes equal in magnitude to the rate of the hydrolysis reaction (maximum on the curve in Fig. 3). Subsequently the hydrolysis process begins to predominate over the sorption process, and the weight of the substance decreases.

Fig. 3. Change in weight of $TiCl_4$ hydrolysis products as a function of residence time in atmospheric air

To study the phase composition of the products obtained by hydrolytic decomposition of $TiCl_4$, the method of X-ray qualitative phase analysis of polycrystalline substances was used (Debye-Scherrer method). It was established that the products of vapor-phase hydrolysis of $TiCl_4$, obtained in the temperature range:

1) 75-150° form a new crystalline phase, previously unknown, with a structure different from the structures of known titanium compounds. This new phase is no longer detected at 300°;

2) 25-50° and ratios of $TiCl_4$: H_2O in the reaction mixture of 1 : 1, 1 : 2, and 1 : 3 show no crystalline structure by X-ray analysis. However, after a short time in moist atmospheric air they acquire an unmistakably crystalline structure, and their interference pattern is close to that shown by the products obtained in the interval 75-150°;

3) 300-750°—are titanium oxide TiO_2 with the anatase structure.

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Note: Figure translations are in progress. See original paper for figures.