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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Reactions of Cobalt Oxide with Chlorine

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Abstract—We report the thermodynamic calculations and experimental studies of the kinetics of the reaction of Co_3O_4 with chlorine at 300–850°C. The show that cobalt chloride sublimation is controlled by the rate of chloride evolution from the surface. The chlorination specifics of the oxides of iron-family metals are compared.

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Anhydrous chlorides of iron-family metals are widely used in engineering and technology, in particular as reagents in inorganic and organic synthesis and as catalysts. The reactions of iron and nickel oxides with chlorine are well understood [1–4]. Cobalt oxide is known to react with chlorine at relatively low temperatures; however, data on low-temperature chlorination of cobalt oxide are rather controversial [5, 6]. Chlorination is a way to prepare pure anhydrous $CoCl_2$, the most widely used cobalt salt.

Here, we report the results of thermodynamic modeling of the system containing cobalt, oxygen, and chlorine and experimental kinetic studies of the reaction between cobalt oxide and chlorine at 300–850°C; we also compare the specifics of this reaction with the chlorination reactions of nickel and iron oxides studied previously [1–4].

The equilibrium compositions of the gas and condensed phases of the Co–O–Cl system with various component ratios were calculated through free-energy minimization using Astra software [7].

Figures 1a and 1b show the equilibrium composition of the gas and condensed phases, respectively, for the stoichiometric component ratio of the reaction

$$Co_3O_4 + 3Cl_2 = 3CoCl_2 + 2O_2$$

In the range 400–600°C, oxygen and chlorine are the main gas-phase components. The $CoCl_2$ partial pressure monotonically increases with temperature to reach 10^{-3} atm at 650°C and 0.3 atm at 1000°C. The condensed phase consists of Co_3O_4 and $CoCl_2$; the Co_3O_4 proportion decreases with increasing temperature. At 900°C cobalt(II) oxide appears in the condensed phase. The cobalt proportion in the oxide decreases with temperature from 42.5% at 400°C to 20.6% at 1000°C. An increase in the chlorine proportion in the batch leads to an increase in the cobalt proportion in the chloride over the whole temperature range. Thus, thermodynamic calculations show that the chlorination of cobalt oxide can occur over a wide temperature range.

Below 600°C the cobalt dichloride partial pressure is negligible; therefore, cobalt chloride sublimation should not occur. $CoCl_2$ accumulation in the condensed phase during the reaction of cobalt oxide with chlorine can create diffusion hindrances to chlorination. High cobalt volatilization is possible at temperatures above 700°C.

Cobalt oxide chlorination kinetics were studied in an isothermal mode on a flow-through setup [8] and on a gravimetric setup with the weight change recorded over time [9]. A high purity grade Co_3O_4 sample (73.4 wt % Co) was used in these experiments. The BET specific surface area of the cobalt oxide sample measured by low-temperature krypton adsorption was 3.5 m^2/g. X-ray powder diffraction and chemical analysis were used to identify the starting sample and reaction products. To determine the product cobalt chloride in the condensed phase, the sample after an experiment was treated with water. Analysis showed that almost all $CoCl_2$ dissolved, and the solid phase was Co_3O_4. Then, cobalt was determined in the solid residue and solution. The difference between the cobalt weight in the starting sample and the overall cobalt weight in the solution and solid residue after the experiment was the amount of cobalt that entered the gas phase in the chloride form.

Isotherms of the degree of cobalt conversion to chloride in the reaction of cobalt chloride with chlorine are plotted in Fig. 2. At 300°C, the conversion does not exceed 5%. At 400–550°C, the conversion increases rapidly for 20–40 min, then the chlorination rate drops. An increase in temperature from 400 to 600°C slightly increases the process rate. At 500–550°C, the degree of cobalt conversion to chloride exceeds 90%. The chlorination rate is high even when considerable amounts of cobalt chloride are formed.

Weight-change versus time isotherms are shown in Figs. 3a and 3b. At 350–550°C the reaction of cobalt

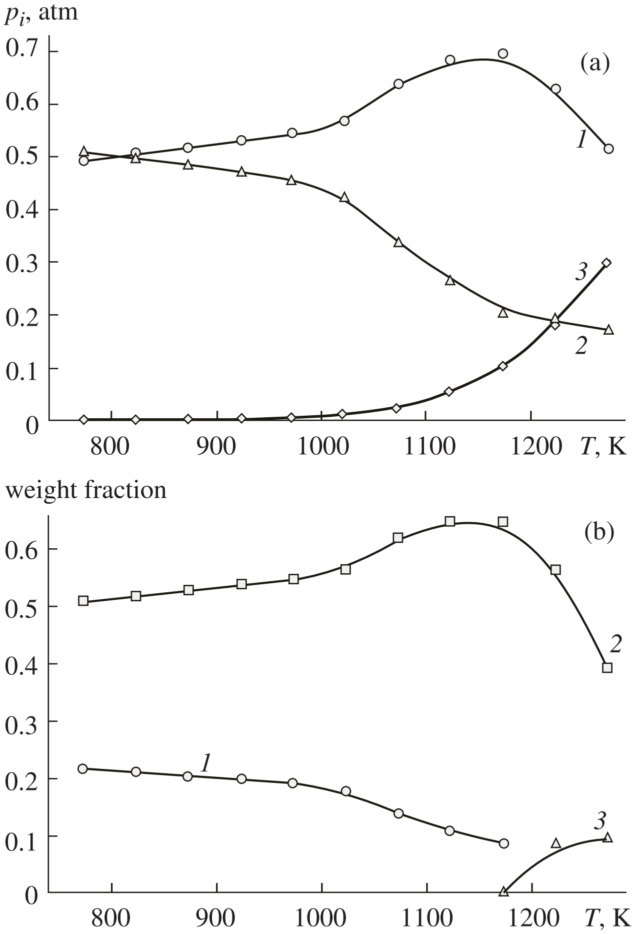

Fig. 1. Panel (a): the equilibrium composition of the gas phase of the $Co_3O_4 + 3Cl_2$ system vs. temperature: (*1*) O_2, (*2*) Cl_2, and (*3*) $CoCl_2$. Panel (b): the same for the condensed phase: (*1*) Co_3O_4, (*2*) $CoCl_2$, and (*3*) CoO.

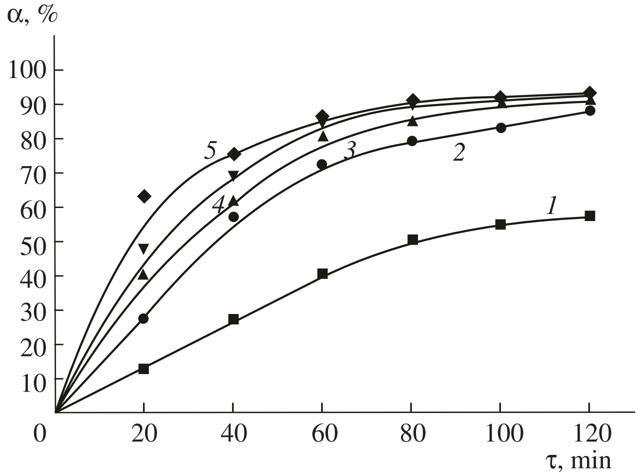

Fig. 2. Co_3O_4 chlorination isotherms at (*1*) 350, (*2*) 400, (*3*) 450, (*4*) 500, and (*5*) 600°C.

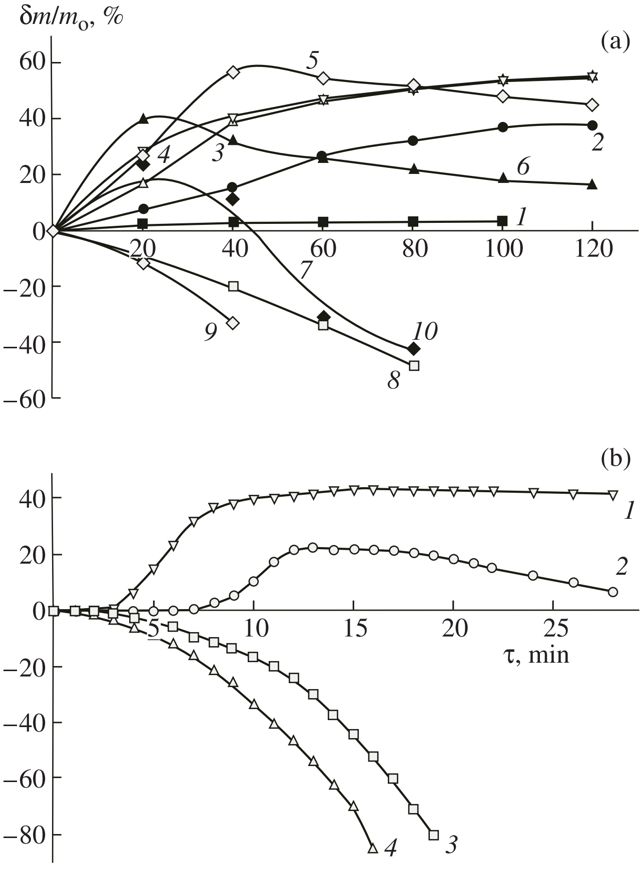

Fig. 3. Panel (a): weight increment vs. run duration in a flow-through setup at (*1*) 300, (*2*) 350, (*3*) 400, (*4*) 500, (*5*) 600, (*6*) 650, (*7*) 700, (*8*) 750, and (*9*) 800°C. Penal (b): the same in a gravimetric setup at (*1*) 600, (*2*) 700, (*3*) 800, and (*4*) 850°C.

oxide with chlorine is accompanied by weight gain only. Cobalt chloride sublimation starts at 600°C, where the degrees of conversion exceed 90%. The weight of the sample decreases as a result of cobalt chloride sublimation. Figure 3b illustrates more details of the initial period of the reaction for 600–850°C. An induction period, whose duration depends on temperature, is observed in all isotherms. At 600°C, weight gain starts after 2 min. At 700°C, the duration of the induction period increases to 8 min, followed by weight gain. After $\Delta m/m_0$ reaches a maximum (20%), which is lower than achieved at 600°C, the weight decreases. It is known that the initial chlorination stage is chlorine chemisorption on the oxide surface. When chlorine chemisorption is the rate-controlling stage of the process, an induction period can appear. No weight change was detected during chemisorption because of the insufficient sensitivity of the investigation method: the weight change of the test sample (0.2 g) after monolayer surface coverage is 4×10^{-4} g, and the sensitivity

Table 1. Cobalt distribution between gas and solid phases

T, °C	Time, min	Cobalt distribution between reaction products, % of the batch concentration			Cobalt conversion to chloride, %
		Co_3O_4	$CoCl_2$ condensed	$CoCl_2$ sublimed	
650	40	35.5	39.4	25.1	64.5
	60	28.7	42.0	29.3	71.3
	100	19.5	46.0	34.5	80.5
700	40	27.8	42.6	29.6	72.2
	60	14.3	47.3	38.4	85.7
	100	10.8	30.4	58.8	89.2
750	40	24.2	40.3	35.5	75.8
	60	11.9	46.6	41.5	88.1
	100	2.7	23.7	73.6	97.3
800	20	23.7	39.5	36.8	76.3
	40	–	–	100.0	100.0
850	20	23.3	24.2	52.5	76.7
	40	–	–	100.0	100.0

of the gravimetric setup is 1×10^{-3} g/mm scale. The chemisorption stage is followed by the formation of a reaction surface layer, in which $CoCl_2$ nucleation occurs. These processes end by the appearance of a new cobalt chloride phase. The chemisorption rate increases with rising temperature. At 700°C, however, the induction period (8 min) is longer than at 600°C (2.5 min). The extent of $CoCl_2$ sublimation increases considerably with temperature (Table 1). From Table 1, which illustrates the cobalt distribution between the reaction products, one can see that the Co_3O_4 concentration in the solid residue at 700–750°C monotonically decreases, the $CoCl_2$ proportion in the sublimate monotonically increases, while the $CoCl_2$ proportion in the condensed phase passes through a peak. This tendency is characteristic of consecutive reactions with an intermediate, in which the formation rate of the intermediate is higher than the formation rate of the final product. In the case at hand, condensed $CoCl_2$ can be considered as an intermediate and sublimed $CoCl_2$ as a final product. The increase in the induction period at 700°C can be due to the competition between the formation of condensed cobalt chloride and its volatilization. Because the $CoCl_2$ formation rate exceeds the sublimation rate, the weight starts to increase after the induction period is over due to accumulation of cobalt chloride in the solid phase. The weight decreases when the extents of cobalt oxide conversion to chloride are higher than 50%. The maximum weight gain and the period of reaching this maximum decrease with temperature elevation. At 800–850°C, weight gain in the initial period of time was not detected. The weight started to decrease after the induction period (2 and 1 min, respectively), and after 20 min cobalt sublimed completely (Figs. 2, 3).

Table 2. Ratio of O_2 and Cl_2 equilibrium partial pressures for the $M_3O_4 + 3Cl_2$ (M = Fe, Co, or Ni) systems

T, °C	p_{O_2}/p_{Cl_2}		
	Fe	Co	Ni
300	1.1×10^{-6}	0.76	7745.2
400	0.2×10^{-5}	0.78	878.9
500	0.4×10^{-4}	0.84	178.9
600	4.0×10^{-4}	0.93	52.7
700	0.004	1.03	18.1
800	0.025	1.65	20.6
900	0.084	2.45	61.0

The chloride sublimation rate at 800–850°C was high, but at short reaction times at these temperatures, the solid phase contained noticeable cobalt dichloride amounts, as indicated by the different extents of reaction and $CoCl_2$ sublimation (Table 1). This confirms that cobalt dichloride formation in the condensed phase until 850°C is an intermediate stage of cobalt chloride sublimation.

Thus, cobalt oxide chlorination at 300–850°C has high rates. At 300–350°C, cobalt chloride pileup on the surface dramatically slows down the process. Above 400°C, virtually all cobalt oxide converts to chloride. The apparent activation energy at 350–550°C is 3.5 kcal/mol. Cobalt chloride volatilization occurs above 600°C. The apparent activation energy at 600–800°C is 20.5 kcal/mol, which is close to the value reported in [5]. $CoCl_2$ sublimation at these temperatures controls the chloride sublimation.

The high cobalt dichloride formation rate in a condensed phase can be due to the $CoCl_2$-mediated race mechanism of chlorine transport to the reaction interface [10]. A similar phenomenon was observed in the reaction between nickel oxide and chlorine [9]. However, unlike Co_3O_4 (an *n*-type semiconductor), nickel oxide is a *p*-type semiconductor, chlorine chemisorption on which enriches the surface layer with charge carriers [11]. It was pertinent to compare the chlorination laws discovered for these oxides with those for a third metal of the same family, namely Fe_2O_3, which has a high electronic conductivity, as Co_3O_4.

Table 2 lists the ratios of O_2 and Cl_2 equilibrium partial pressures for the systems $M_3O_4 + 3Cl_2$, where M = Fe, Co, or Ni. These ratios indicate that the chlorine affinity correlates with the position of the metal in the Periodic Chart, increasing in the following order: Fe < Co < Ni. The equilibrium pO_2/pCl_2 value in the Co–O–Cl system is several orders of magnitude higher than in the Fe–O–Cl system and several orders of magnitude lower than in the nickel system. This distinction diminishes with rising temperature.

Chlorination rates were compared for the most abundant iron-family metal oxides: Fe_2O_3, Co_3O_4, and NiO. The reactions of cobalt and nickel oxides with chlorine obey similar kinetic laws: chloride phases appear at as low temperature as 300°C; chloride sublimation occurs at higher temperatures. Fe_2O_3 chlorination starts at 600°C, and nascent iron chloride is immediately volatilized [3]. The iron chloride sublimation rate, unlike that for nickel and cobalt oxides, is controlled by the surface reaction layer, whose rearrangement generates iron trichloride. Thus, the key role in chlorination is played by the fact that the valence +3 is not intrinsic to cobalt and nickel in their simple compounds (whereas for iron these salts are most stable), and not by the electrophysical properties of iron-family oxides. According to the literature [4], iron oxides (FeO and Fe_3O_4) under a chlorine atmosphere transform to Fe_2O_3; the chlorination product is $FeCl_3$. Despite the fact that cobalt in Co_3O_4 has two valences, this oxide does not convert to Co_2O_3 under a chlorine atmosphere, and $CoCl_2$ is the only stable cobalt chloride.

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