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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

The Regular Features of Chlorine Formation in the Systems NaCl–Me_xO_y–O_2 and Ca(Zn)Cl_2–Me_xO_y–O_2

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Abstract—The reaction of sodium, calcium, and zinc chlorides with atmospheric oxygen in the presence of transition metal oxides and antimony oxide at temperatures exceeding the melting temperatures of chlorides was studied. The content of chorine, product of oxidation of chloride ions in molten NaCl and $CaCl_2$, was determined as a function of the polarization force of cations of transition metal oxides.

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The heterogeneous-catalytic oxidation used for neutralization of chlorine-containing organic substances yields chlorine and hydrogen chloride, which react with the components of a solid-phase catalyst and cause its destruction or deactivation.

For certain molten catalytic compositions, the reaction with Cl_2 and HCl is reversible [1], which can be used in development and regeneration of catalysts. Therefore, we studied the oxidation of chloride ions in the Na(Ca, Zn)$Cl_{(2)}$–M_xO_y–O_2 systems, where M_xO_y is transition metal oxide and antimony(V) oxide.

The oxidation of halide ions in a melt of metaphosphates in the presence of atmospheric oxygen has been studied in [2, 3]. The reaction of Na(K)Cl with V_2O_5 at 400–600°C in air can be used for synthesizing sodium and potassium metavanadates [4–6]. A method has been proposed [7] to produce chlorine and calcium oxide by oxidation of calcium chloride with atmospheric oxygen at 800°C. The oxidation of chloride ions with permanganate ions, including that with joint action of ozone, has been studied in [8, 9]. The introduction of metaphosphates [2] and transition metal oxides [10] into the NaCl melt promotes oxidation of chloride ions.

EXPERIMENTAL

We used in the experiments NaCl, $ZnCl_2$, $CaCl_2$, MoO_3, CrO_3, Sb_2O_5, V_2O_5 (all of chemically pure grade) and analytically pure CuO. The air (nitrogen) was bubbled through the solution or passed over the surface of the reaction mixture. The content of released chlorine was determined iodometrically by passing it through a solution of potassium iodide and titration of the formed amount of I_2 with sodium thiosulfate solution. The method of performing the experiments has been described in detail in [11].

The X-ray phase analysis (XPA) was performed at room temperature in air [Rigaku diffractometer D_{max} = 2200/PC), CuK_α radiation, λ = 1.5418 Å]. The presence of certain elements in the reaction products was confirmed by the thermal and flame atomic absorption spectroscopies (GBC 908AA spectrometer).

In air flow, chlorine starts to separate from calcium chloride at 380°C, i.e., below the melting point (T_m = 772°C) and from $ZnCl_2$ it starts to separate above 400°C, i.e., above the melting point (317°C). In an air flow of 2.5 l h^{-1}, no chlorine is separated from sodium chloride at 800–820°C, whereas from $ZnCl_2$, 0.00289 moles of Cl_2 per 1 mole of $ZnCl_2$ is separated at 580°C in 8 h. The amount of chlorine formed by the reaction of calcium chloride with atmospheric oxygen at 700°C in 5 h is considerably less (0.00897 moles of Cl_2 per 1 mole of $CaCl_2$).

The specific amount of chlorine (moles of Cl_2 per 1 mole of oxide) formed in the NaCl–V_2O_5, NaCl–MoO_3, and NaCl–Cr_2O_3 systems at 800°C is independent of concentration of the oxides in the range

5–30 wt %. At the same time, in the system $ZnCl_2$–Cr_2O_3 at 500°C the specific amount of forming chlorine decreases, as the concentration of Cr_2O_3 in the melt is increased from 5 to 10 wt %.

The activity of the studied compounds in oxidation of chloride ions in the NaCl melt decreases in the order [10]: $CrO_3 > V_2O_5 > MoO_3 > Sb_2O_5 > CuO > Co_3O_4$.

In deep oxidation of H_2, CO, and hydrocarbons, the catalytic activity of solid-phase metal oxides is determined by the bond energy of oxygen. The lesser the bond energy (heat of oxygen desorption), the higher the catalytic activity of the oxide [12, 13]. The metal oxides are arranged in the following order with respect to the specific activity in the indicated reactions: $Co_3O_4 > CuO > MnO_2 > NiO > Fe_2O_3 > ZnO > Cr_2O_3 > V_2O_5 > TiO_2$. This order coincides with the order of increasing the oxygen bond energy and is opposite to the above-presented order of the oxide activity in oxidation of chloride ions.

The oxidation of chloride ions in the NaCl–M_xO_y system is due to the activation of atmospheric oxygen with transition metal oxides [10, 11]. Chlorine oxidation with V(V), Cr(VI), Mo(VI), and Sb(V) oxides in an inert atmosphere is also possible owing to reduction to ions with the lower oxidation degrees or to the formation nonstoichiometric oxygen of compounds. The latter is typical of vanadium pentoxide [14, 15], including the case when it is incorporated into the composition of catalysts due to redox reactions $V^5 \rightleftarrows V^{4+}$ [16–18]. For example, Vol'fson et al. [19] established that the active components of a vanadium oxide catalyst for naphthalene oxidation are lower vanadium oxides V_2O_4 and V_6O_{13} (the latter contains 64.4 wt % of V_2O_4). The optimal composition of the catalyst for partial oxidation of ethanol on molten K_2O–V_2O_5 system corresponds to the formula $K_2V_8O_{(21-x)}$ (vanadium oxide bronze) [20].

Pastukhov et al. [16] determined that for vanadium pentoxide (V_2O_{5-x}), a constituent of the oxide mixture, the degree of oxygen nonstoichiometry depended on temperature, partial oxygen pressure, and on the size and polarization force, $ze/r_{M^{z+}}$, of the introduced cation, where z was the ion charge and r, its radius. The higher the $ze/r_{M^{z+}}$, the larger the $\Delta G0$ of oxide formation, a characteristic of the cation affinity for oxygen. According to the data of the X-ray phase analysis, the introduction of large single and double charged cations with small polarization force into the molten vanadium pentoxide causes interatomic V–O space to decrease from 0.018 to 0.017 nm in the presence of K^+ cations (r = 0.133 nm) [21]. As the V–O bond becomes stronger, vanadium pentoxide dissociation and the concentration of V^{4+} ions decrease, i.e., the reduction ability with oxygen evolution decreases.

In oxide melts, contrary to the case of salt systems, the contribution of covalent bond to bonding between atoms is considerable [21], i.e., both the covalent and the ionic bonds exist. In the NaCl melt, which is a ionic liquid, the ionic bond, especially at low oxide concentrations, dominates.

Kochergin et al. [2] accounted for the regularity of change in the amount of forming chlorine in melts of alkali metal chlorides and calcium chloride during reaction with atmospheric oxygen in the presence of metaphosphates by ascribing it to the polarizing effect of the salt cations z/r^2. The activity of transition metals in Cl^- oxidation in the NaCl melt correlates with the sizes of the ionic radii [22] and with a polarization force of the cation, $ze/r_{M^{z+}}$, as follows from the data of Table 1.

The dependence of the chlorine amount $N(Cl_2)$ formed in the NaCl–M_xO_y system on the polarization force of the oxide cation is described by the equation

$$N(Cl_2) = 0.5422x - 0.0679$$

with a correlation coefficient of 0.9899.

In the presence of two or three oxides in the system, the synergistic effect is not observed. In this case, on the contrary, the activity of mixed metal oxides in oxidation of chloride ions is inhibited in comparison with the activity of individual oxides. The activity of mixed oxides was calculated from the additivity law. A decreased activity of the oxide mixtures in oxidation of chloride ions in comparison with the activity of individual oxides (Table 2) can be also attributed to the polarization force of cations.

The chlorine amount formed upon Cl^- oxidation in the system constituted by two or three oxides depends virtually linearly on the sum of the polarization forces, $ze/r_{M^{z+}}$, of the oxide cations introduced into the sodium chloride melt in terms of their mole fraction per one cation. For example, the polarization force of cations in the CrO_3–V_2O_5 mixture (components ratio 2:1) is $(2\cdot0.82 + 0.60)/2 = 0.75$. The equation for the $N(Cl_2)$–$ze/r_{M^{z+}}$ dependence, where M_{z+} is the oxide cation introduced into the NaCl–V_2O_5 system has the form

$$N(Cl_2) = 0.7007x - 0.2318.$$

Table 1. Ionic radius, polarization force of cations, and chlorine amount formed in the MeCl–M_xO_y[a] system

Cation	Cr^{6+}	V^{5+}	Mo^{6+}	Sb^{5+}	Mn^{4+}	Cr^{3+}	$Co^{2+, 3+}$	Cu^{2+}	Zn^{2+}
$r_{M^{z+}}$, nm	0.035	0.040	0.065	0.062	0.052	0.064	0.064 (Co^{3+}) 0.078 (Co^{2+})	0.080	0.083
$ze/r_{M^{z+}}$, ESU cm^{-1}	0.82	0.60	0.44	0.39	0.37	0.23	0.23 (Co^{3+}) 0.12 (Co^{2+})	0.12	0.12
M_xO_y	CrO_3	V_2O_5	MoO_3	Sb_2O_5	MnO_2	Cr_2O_3	Cr_2O_3	CuO	ZnO
	NaCl–Me_xO_y								
	0.365	0.291	0.156	0.132	–	–	0.001	0.002	–
Cl_2 amount, moles of Cl_2 per mole of oxide	$ZnCl_2$–Me_xO_y								
	–	0.031	0.021	0.036	0.031	0.039	0.004[b]	0.009	0.003
	$CaCl_2$–Me_xO_y								
	0.356	0.461	0.067	0.110	–	0.038	–	0.010	-

[a] Heating: for NaCl from 20 to 820°C, for $ZnCl_2$ to 500°C, for $CaCl_2$ to 700°C and then at 820, 500, or 700°C and in an air flow of 2.5 l h^{-1} over the mixture surface during 300 min. [b] CoO.

In this case, the correlation coefficient (r = 0.9186) is worse than for individual oxide.

Among the oxides studied, the highest polarization force has V^{5+}, except for Cr^{6+}. Therefore, the introduction of cations, whose ionic radii are larger than the radius of vanadium cation, into the system decreases the ability to form oxygen-nonstoichiometric compounds and to activate the gas-phase oxygen. There is observed a pronounced tendency: the larger the radius and the lesser the polarization force of the introduced cation, the lower the activity of oxides for the chlorine formation. Probably, in a mixture of CrO_3 and V_2O_5 the opposite polarization effect exerted by V^{5+} ions decreases the activity of chromium (VI) oxide. This explains why the experimentally found value deviates from the correlation line. The experimental values of the chlorine amount formed in the presence of the Sb_2O_5–V_2O_5 mixture virtually coincide with the calculated value from the additivity law. This is due to the covalent bonding in Sb_2O_5.

At the background of calcium ions, whose polarization force is larger than that of sodium ions, the effect exerted by metal oxides on the oxidation of chloride ions is lesser (Table 1) and chlorine formation is inhibited by the metal oxides (Co_3O_4, CuO) whose cations have a polarization force comparable to that of calcium ions. The introduction of oxides (MoO_3, Sb_2O_5, Cr_2O_3, CuO) into the $CaCl_2$ melt decreases the amount of chlorine formed in the air flow. The XPA revealed chromium oxide in the $CaCl_2$–Cr_2O_3 system, copper oxide in the $CaCl_2$–CuO system, and no oxides in mixtures with sodium chlorides.

The presence of complex ions in calcium-containing halide melts, e.g., the presence of $[CaCl]^+$, $[CaCl_3]^-$, and $[CaCl_4]^{2-}$ in the calcium chloride melt, has been demonstrated in [23]. The presence of oxygen ions O^{2-} formed in the melt upon oxidation of chloride ions by reaction [23]

$$O_{2(g)} + 4Cl^- \rightleftarrows 2O^{2-} + 2Cl_{2(g)},$$

changes the inner coordination sphere of the complex ions of composition $[Ca_2OCl_n]^{n-2}$ having Ca–O–Ca bridging bonds [24]. When the oxides whose metal cations have a polarization force equal or lower than the polarization force of calcium ion, $ze/r_{Ca}2+$, are introduced into the melt, the Ca–O and Ca–Cl bond strength increases. As a result, the amount of chlorine separated in an air flow over the melt decreases.

The $N(Cl_2)$–$ze/r_{M^{z+}}$ dependence is described by the equation $N(Cl_2) = 0.4964x - 0.0806$, r = 0.9546, with vanadium pentoxide not taken into account in Cl^- oxidation in the $CaCl_2$ melt. Note that chlorine amount formed in the $CaCl_2$–V_2O_5–O_2 system is larger that that corresponding to the above dependence, which may be due to the reaction of calcium oxide formed upon $CaCl_2$ oxidation with V_2O_5. According to the calculations, the amount of calcium oxide formed upon $CaCl_2$ oxidation in a mixture constituted by $CaCl_2$ (27 g) and V_2O_5 (3 g) can react with 1.38 g of V_2O_5 to form the compound of composition CaO V_2O_5, which

Table 2. Polarization force of the cation mixture and Cl_2 amount formed (calculated) in the $NaCl–V_2O_5–M_xO_y$ system

Oxides, molal ratio	$\frac{\Sigma ze/r_{M^{z+}}}{nM^{z+}}$, ESU cm^{-1}	Cl_2 amount, moles of Cl_2 per 1 mole of the oxide
$CrO_3–V_2O_5$, 2:1	0.75	0.2448 (0.3418)
$MoO_3–V_2O_5$, 2:1	0.49	0.1376 (0.2176) bubbling
$Sb_2O_5–V_2O_5$, 1:1	0.50	0.1909 (0.2110)
$CuO–V_2O_5$, 1:1	0.36	0.0533 (0.1494)
$CuO–V_2O_5$, 2:1	0.28	0.0081 (0.0983)
$Sb_2O_5–V_2O_5–CuO$, 1:1:1	0.37	0.0467 (0.1430)

Table 3. Oxidation rate constants for chloride ions in the systems $NaCl–V_2O_5$ and $ZnCl_2–V_2O_5$ in an air flow of 2.5 l g^{-1}

Reaction	$k\times10^5$, s^{-1}
$7NaCl + 5NaV_6O_{15} + 2.4O_2 = 6Na_2V_5O_{13.3} + 3.5Cl_2$: Air–bubbling, 880°C	13.10 ± 0.13 [11]
Air–bubbling, 820°C	8.00 ± 0.20 [11]
Air flow over the melt surface,820°C	1.01 ± 0.03 [11]
$3ZnCl_2 + V_2O_5 + 1.5O_2 = Zn_3(VO_4)_2 + 3Cl_2$: Air flow over the melt surface, 650°C	0.16 ± 0.02
Air flow over the melt surface, 500°C	0.09 ± 0.02

forms eutectics with V_2O_5 (taken in approximately equimolar amount). Chekryshkin et al. [20] point to the fact that in the melts of CaO with V_2O_5 the bonds V–O–V are substituted for the V–O–Ca bonds with larger degree of ionicity. As a result, the mobility of calcium cations and the rate of the Cl^- oxidation increase. In the system $CaCl_2–V_2O_5$, the compound of composition Ca_2VO_4Cl is formed after passing the air through the melt according to the data of XPA.

The linear dependence of chlorine amount formed upon Cl^- oxidation in the $Na(Ca,Zn)Cl_{(2)}–M_xO_y$ system on the polarization force of the oxide cation shows that the reaction proceeds by the ionic mechanism. After substituting the sodium and calcium chlorides for zinc chloride, which belongs to covalent associated melts [21], the order, in which metal oxides are arranged with respect to their activity in oxidation of chloride ions, is changed (Table 1). The correlation dependence is described by the equation

$$N(Cl_2) = 0.0529x - 0.0061,$$

where x is the polarization force of the cation and r = 0.6555.

The $N(Cl_2)$ and electronegativity of elements (cations), χ^2/r_O, are in even worse correlation (–0.2853).

Chlorine amount formed in the system $ZnCl_2–M_xO_y–O_2$ is less than in the $NaCl–M_xO_y–O_2$ system and the oxide activity decreases in the order: $Cr^{3+} > Sb^{5+} > V^{5+} \approx Mn^{4+} > Mo^{6+} > Cu^{2+} > Co^{2+} > Zn^{2+}$ (Table 1).

The small range, wherein the chlorine amount formed in the $ZnCl_2$ melt changes, shows that the effect exerted by the type of transition metal oxide on the Cl^- oxidation is slight. Thus, the larger the polarization force of the chloride cation, the lesser the effect exerted by the oxides on the specific amount of forming chlorine (moles of Cl_2 per mole of M_xO_y), i.e., the lesser the sensitivity of chloride ion oxidation to the type of oxide cation.

The X-ray phase analysis of the reaction systems after the Cl^- oxidation revealed CuCl, in addition to $ZnCl_2$, in the system $ZnCl_2$–10 wt % CuO and, and only $Zn_3(VO_4)_2$ in the $ZnCl_2–(VO_4)_2$ system. The XPA of a sample of the $ZnCl_2$–10 wt % Sb_2O_5 system kept in air flow for 300–500 min confirmed zinc chloride and antimony oxide Sb_2O_5. Evidently, another compounds formed in the systems are X-ray amorphous.

The rate constants of Cl^- oxidation in the systems $NaCl–V_2O_5–O_2$ and $ZnCl_2–V_2O_5–O_2$ were calculated as pseudo-first-order reaction (Table 3).

As seen from the data of Table 3, the oxidation rate of chloride ions in the NaCl melt is higher that in the $ZnCl_2$ melt. This may be due to the difference in the experimental conditions and due to the effect exerted by the type of metal cation. The kinetics of the reaction of metal oxides with NaCl was studied by bubbling air through the melt, i.e., at intense agitation of the reaction mixture. The $ZnCl_2–M_xO_y$ mixtures were brought into contact with oxygen through the air passing over the melt surface. For this scheme of the process, the oxidation rate of chloride ions in the melt is controlled by diffusion, as confirmed by the low activation energy of oxidation. The apparent energy of Cl^- oxidation is 109 kJ mol^{-1} for sodium chloride melt and 28 kJ mol^{-1} for zinc chloride melt.

The dynamics of chlorine separation from the $ZnCl_2$–V_2O_5 melt is also described by the zero-order equation [$k = (0.12 + 0.03)\times10^{-6}$ mol s^{-1} at 500°C], with activation energy of the process virtually zero. This shows that the oxidation rate of chloride ion is higher than the diffusion rate of chlorine from the melt into the gas phase.

CONCLUSIONS

(1) The oxidation of chloride ions with atmospheric oxygen in melts of sodium, calcium, and zinc chlorides in the presence of transition metal oxides depends on the type of chloride and oxide cations.

(2) The high correlation coefficients for the dependence of the amount of separating chlorine on the polarization force of the oxide cations in sodium and calcium chlorides are accounted for by their ionic structure. The covalent bond in $ZnCl_2$ is responsible for the lack of the above dependence.

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