Mechanism of the Formation of Carbon Oxides under Conditions of the Oxidative Chlorination of Methane: III. Kinetics of the Reaction of CCl_4 with Oxygen on Copper-Containing Salt Catalysts

A. G. Aglulin and N. A. Kostikov

Karpov Institute of Physical Chemistry, Moscow, 105064 Russia
*e-mail: fn_@rambler.ru*
Received January 11, 2008

Abstract—The kinetics of the oxidative dechlorination of CCl_4 on two supported catalysts for methane oxychlorination ($CuCl_2$–KCl and $CuCl_2$–KCl–$LaCl_3$) at 350–425°C was studied using a gradientless method. Although these catalysts exhibited different activities, the rate of reaction on them was described by one exponential equation at the same activation energy of $E \approx 26.3$ kcal/mol. A two-path reaction mechanism was proposed, which involved the dissociative adsorption of initial reactants and chlorine with the formation of phosgene and the oxidation of phosgene to CO_2. The occurrence of two types of active sites on the catalyst surface was assumed.

INTRODUCTION

The reactions of CCl_4 with oxygen to form carbon dioxide and, probably, phosgene

$$CCl_4 + O_2 = CO_2 + 2Cl_2, \qquad (I)$$

$$CCl_4 + 1/2O_2 = COCl_2 + Cl_2 \qquad (II)$$
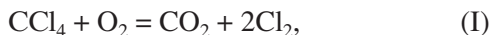
on supported copper-containing salt catalysts for the oxidative chlorination of methane were studied in order to complete previous kinetic studies [1, 2] of the oxidation paths of methane and chloromethanes in the reaction

$$CH_4 + n/2O_2 + nHCl = CH_{4-n}Cl_n + nH_2O. \qquad (III)$$

Aglulin [1, 2] was the first to find a dramatic effect of the partial pressure of chlorine (P_{Cl_2}) in the reaction mixture on the chemical and phase compositions of copper-containing salt catalysts and their catalytic properties. The observed changes in the kinetics and mechanism of side reactions at $P_{Cl_2} < 0.1$ kPa were explained by the conversion of copper chloride as a catalyst constituent into an oxide–oxychloride form under these conditions.

We did not specially study the oxidation of CCl_4 under conditions of reaction (III). However, Aglulin [2] found that the oxidation of CCl_4 can considerably contribute to the formation of carbon dioxide as a by-product in reaction (III). According to a preliminary estimation, the rate of the reaction of CCl_4 with oxygen is higher than the rate of oxidation of methyl chloride, which is the most reactive among the other three chloromethanes. Thus, information obtained previously [1, 2] is insufficient to describe the formation of carbon oxides as by-products in the reaction of methane oxychlorination.

EXPERIMENTAL

Kinetic experiments were performed in a fixed bed of supported copper-containing salt catalysts using a flow circulation method [3]. Two salt systems ($CuCl_2$–KCl and $CuCl_2$–KCl–$LaCl_3$; the molar ratios between the components were 1 : 1 and 1 : 1 : 0.33, respectively), which were supported from aqueous solutions onto porous supports with a grain size of 0.25–0.5 mm, were used. DN-2 diatomite and KSK-2 and KSKG silica gels were used as the supports. Their specific surface areas were 1.5, 340, and 350 m^2/g at average pore diameters of ~1500, 140, and 120 Å, respectively [4]. For comparison, oxide analogs of the above catalysts were used. The catalysts were prepared by the impregnation of the supports with aqueous solutions of copper nitrate, potassium chloride, and lanthanum chloride. After drying at room temperature (12–20 h) and then at 80–120°C (~4 h), the samples were calcined at 400–450°C until the complete removal of nitrogen oxides.

CCl_4 was introduced into a heated loop from a thermostatically controlled saturator, through which a flow of gaseous nitrogen was passed. Analytical grade CCl_4 was used; it was distilled and dried with zeolite CaA. This zeolite was also used for drying oxygen and zero nitrogen. Chlorine (99.8%) was dried using concentrated sulfuric acid of reagent grade.

Table 1. Changes in the initial copper content of the $CuCl_2$–KCl–$LaCl_3$ catalyst (1 : 1 : 0.33) supported on KSK-2 and in the activity of this catalyst in the course of the oxidative dehydrogenation of CCl_4 at 425°C

Reaction time, h	Cu content, wt %	P_i, kPa					Rate of product formation $r_i \times 10^6$, mol g_{Cat}^{-1} h^{-1}			$k \times 10^6$, mol g_{Cat}^{-1} h^{-1} $kPa^{-0.5}$
		CCl_4	O_2	Cl_2	CO_2	$COCl_2$	CO_2	$COCl_2$	Σ	
1.5	2.8	3.70	4.46	9.44	4.6	0.71	1045	161	1206	912
3	~2.4	3.77	4.67	8.45	4.13	0.58	951	134	1085	752
~4.5	~1.8	2.80	28.6	10.2	5.07	0.27	1451	76	1527	547

Note: The quantity $k = r_\Sigma [P_{Cl_2}/(P_{O_2} P_{CCl_4})]^{0.5}$ plays the role of the rate constant of reaction (see below).

To analyze the reaction mixture, we used, for the most part, the previously described procedure [1]. By turning a heated corrosion-resistant six-way valve [5] at the loop outlet, the reaction mixture was sampled and the samples were directed to analysis using two parallel-connected KhT-7 and KhT-8 chromatographs. On combining two individual chromatograms to form a whole, the ratio between the areas of common peaks in either of them was taken into account.

Chromatographic analysis was somewhat modified because it was necessary to monitor the presence of perchloroethylene and hexachloroethane in the reaction mixture and to study the reaction of CCl_4 oxidation in the presence of methane. In the KhT-7 chromatograph, the column with Porapak Q was replaced by a 3-m column with 20% SE-30 on Celite 545 (40–60 mesh). On this column, the reaction mixture was analyzed for the chlorine derivatives of C_1 and C_2 under conditions of temperature programming from 30 to 150°C. Light gases were analyzed on the KhT-8 chromatograph at room temperature. Unlike the procedure [1], both arms of a thermal-conductivity detector were used. The sample was successively passed through columns with Porapak Q (column length $L = 1.5$ m) and molecular sieves 13X ($L = 2$ m), which were separated by a so-called holdup volume. The presence of the holdup volume as a polyvinyl chloride tube ($L = 40$–50 m; diameter, 2 mm) allowed us to separate in time signals from both arms of the thermal-conductivity detector. Difference in sensitivity was controlled by comparing methane peak areas on either of the columns.

Having a combined chromatogram and measuring the flow rate of light gases at the outlet of traps for heavier components, we could determine the volume velocities (V_i) of the majority of reaction mixture components at the outlet of the reaction loop. As previously [1], the volume velocity of Cl_2 was determined by iodometry. The previously described procedure [1] for the determination of chlorine and hydrogen chloride was found applicable to analysis for phosgene. Phosgene was determined from the amount of HCl formed upon phosgene hydrolysis in traps with an aqueous solution of potassium iodide. Yamada and Kanetaki [6]

described a similar procedure for the determination of phosgene in gas mixtures using a trap filled with an aqueous alcohol solution. Under conditions of our experiments, both of these analytical procedures for phosgene were found equivalent. The presence of ethanol in a trap with an aqueous solution of potassium iodide had no effect on the results of iodometric analysis for chlorine. Carbonic acid had a minimum interfering effect on the results of hydrogen chloride titration because, in the majority of experiments, the partial pressure of carbon dioxide was low ($P_{CO_2} < 5$ kPa). In all of the experiments, material balances on CCl_4 and oxygen were obeyed; deviations were no greater than 5%.

To eliminate the effect of deactivation on the numerical values of reaction rate parameters, the catalysts were replaced by fresh portions after operation for 30–35 h at 375°C or 10–12 h at 400°C. The kinetic experiments could be performed for only ~2 h because of a noticeable volatility of copper chloride under reaction conditions at 425°C (Table 1).

RESULTS AND DISCUSSION

The rate of oxidative dechlorination of CCl_4 (r_Σ) per gram of the catalyst was calculated from the sum of the rates of formation of carbon dioxide and phosgene. The formation of hexachloroethane and tetrachloroethylene (perchloroethylene), as well as the possible recombination products of $\dot{C}Cl_3$ and $\ddot{C}Cl_2$ radicals, was not detected. This fact suggests the absence of conditions for nucleophilic substitution like $CCl_3^- + CCl_4 = C_2Cl_6 + Cl^-$ [7] from the reaction zone. Signs of the heterogeneous degradation of CCl_4 to carbon, which can occur in some cases [8], were also absent. The thermal stability of phosgene in the reaction zone was supported by the absence of carbon monoxide from the products. As expected according to the stoichiometry of reactions (I) and (II), the ratio between the volume rates

Table 2. Effect of the specific surface area of the CuCl$_2$–KCl catalyst (1 : 1) with a copper content of ~7 wt % on the rate and the rate constant of the oxidative dechlorination of CCl$_4$ at 375 and 400°C

Support	S_{sp}, m^2/g	T, °C	P_i, kPa					$r_i \times 10^6$, mol g$_{Cat}^{-1}$ h^{-1}			$k \times 10^6$, mol g$_{Cat}^{-1}$ h^{-1} kPa$^{-0.5}$
			CCl$_4$	O$_2$	Cl$_2$	CO$_2$	COCl$_2$	CO$_2$	COCl$_2$	Σ	
DN-2 diatomite	1.5	375	13.2	19.3	2.80*	0.32	0.04	53	7	60	6.35
KSK-2 silica gel	340	375	8.2	42.7	4.75	2.41	0.28	910	106	1016	118
KSKG silica gel	350	375	14.5	40.2	4.80	2.10	0.27	777	100	877	79.3
DN-2 diatomite	1.5	400	12.1	16.9	2.63*	0.60	0.12	96	19	116	13
KSK-2 silica gel	340	400	7.9	12.1	4.56	2.25	0.31	973	134	1107	242

* Experiments with additional introduction of chlorine into the reaction zone.

Table 3. Dependence of the rate of CCl$_4$ oxidation at 375°C on the catalyst composition and the copper content of the catalyst (support: KSK-2 silica gel)

Catalyst	Ratio between components	Cu content, wt %	P_i, kPa					r_i, mol g$_{Cat}^{-1}$ h^{-1}			$k \times 10^6$, mol g$_{Cat}^{-1}$ h^{-1} kPa$^{-0.5}$
			CCl$_4$	O$_2$	Cl$_2$	CO$_2$	COCl$_2$	CO$_2$	COCl$_2$	Σ	
CuCl$_2$–KCl	1 : 1	1.75	21.8	5.9	3.57	1.45	0.45	138	43	181	30.1
CuCl$_2$–KCl	1 : 1	7.0	5.8	12.9	3.90	1.71	0.54	385	123	508	116
CuCl$_2$–KCl–LaCl$_3$	1 : 1 : 0.33	1.6	23.7	13.5	4.10	2.20	0.20	926	84	1010	114
CuCl$_2$–KCl– LaCl$_3$	1 : 1 : 0.33	2.8	23.8	16.9	6.41	3.25	0.45	1611	179	1790	226

of product formation was obeyed with an average deviation of ~6%:

$$2V_{CO_2} + V_{COCl_2} = V_{Cl_2}. \qquad (1)$$

The interaction of CCl$_4$, as well as other chloromethanes [1, 2], with oxygen under conditions of reaction (III) is a heterogeneous catalytic process. This follows from the dependence of the rate of reaction on the specific surface area (S_{sp}) of the support (Table 2). This dependence and the effect of catalyst composition on the rate of reaction (Table 3) can be characterized by comparing the numerical values of reaction rate constants obtained in various experiments. The rate constants were calculated from exponential equation (2) (see below), which describes the kinetics of reaction on both of the catalysts. Comparatively moderate dependence of catalyst activity on the specific surface area of the support suggests that the working surface area of a salt component of the supported system increases with S_{sp} to a much lesser extent. The same character of the dependence under consideration in the oxidation of other chloromethanes [1, 2] is consistent with data on the surface state of copper-containing salt melts in supported catalysts for hydrocarbon oxychlorination and the Deacon reaction [9]. The low surface areas of salt catalyst components were explained by the nonuniform distribution of these components over the surface [9]. This makes it possible to practically exclude the partic-

ipation of small pores and a portion of medium pores of the support in the formation of a supported system and to explain different reaction rates on catalysts with KSK-2 and KSKG silica gels (Table 2), which mainly differ in pore diameter distributions [4].

The rate of reaction depends on not only the specific surface area of the support but also the composition of the salt catalyst. The introduction of 0.33 mol of lanthanum chloride into an equimolar mixture of copper and potassium chlorides increased the catalyst activity per unit weight of copper by a factor of 4.4. However, the catalytic activity of both of the salt systems was almost proportional to the copper content of the system (Table 3).

The kinetic experiments were performed on CuCl$_2$–KCl (1 : 1)/KSK-2 and CuCl$_2$–KCl–LaCl$_3$ (1 : 1 : 0.33)/KSK-2 catalysts with copper concentrations of 7.0 and 2.8 wt %, respectively. As in the oxidation of other chloromethanes [1, 2], the small particle size (0.25–0.5 mm) of the catalysts was responsible for the occurrence of reaction in the kinetic region. The kinetics of the interaction of CCl$_4$ with oxygen was studied at 350–425°C. The partial pressures of CCl$_4$, oxygen, and chlorine were varied over the ranges of 0.6–25, 0.8–60, and 1–11 kPa, respectively. The partial pressures of carbon dioxide varied from 0.2 to 4.5 kPa.

It is difficult to determine rate laws by directly evaluating orders of reaction with respect to reactants using
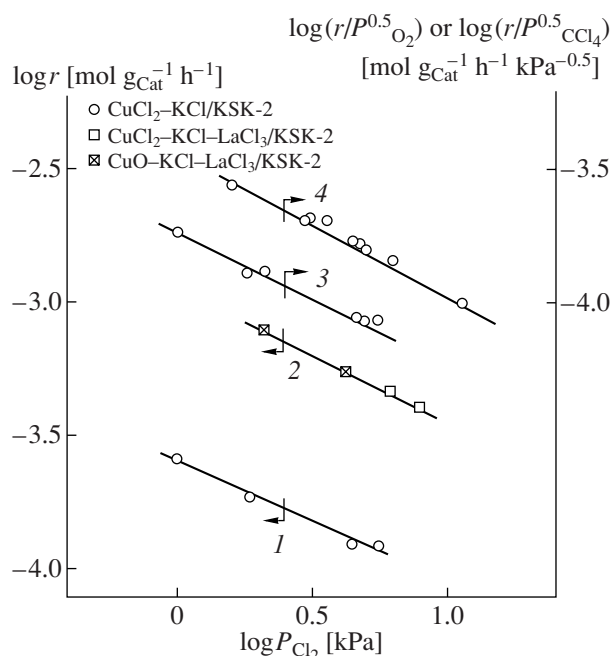
Fig. 1. Kinetic orders of reaction with respect to Cl_2 on copper-containing salt catalysts at reaction temperatures of (1, 3) 350 and (2, 4) 375°C: (1) P_{O_2} = 16.5 and P_{CCl_4} = 2 kPa; (2) P_{O_2} = 20 and P_{CCl_4} = 1.5 kPa; (3) P_{O_2} = 17 kPa; and (4) P_{CCl_4} = 9 kPa.
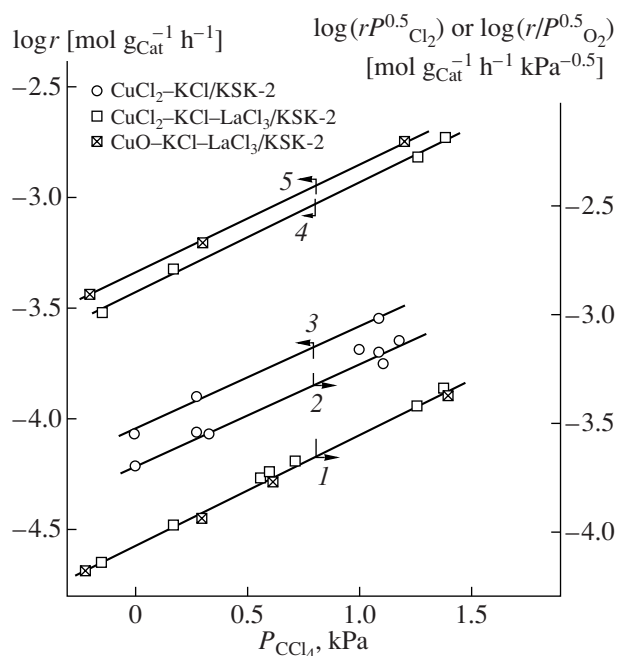
Fig. 2. Kinetic orders of reaction with respect to CCl_4 on copper-containing salt catalysts at reaction temperatures of (2, 3) 350 and (1, 4, 5) 375°C: (1) P_{Cl_2} = 6.2 kPa; (2) P_{O_2} = 17 kPa; (3) P_{O_2} = 17 and P_{Cl_2} = 5 kPa; (4) P_{O_2} = 20 and P_{Cl_2} = 6.2 kPa; and (5) P_{O_2} = 20 and P_{Cl_2} = 4.2 kPa.

a common method because the concentrations of reaction mixture components are interdependent. This manifests itself under any detectable change in the partial pressure of one of these components. Thus, we additionally introduced chlorine into the reaction zone along with changes in the relative residence time.

Common rate laws were observed in the oxidative dechlorination reactions of CCl_4 on copper–potassium catalysts without and with $LaCl_3$. The kinetic order with respect to chlorine was close to –0.5 (Fig. 1), whereas the orders with respect to CCl_4 (Fig. 2) and oxygen (Fig. 3) were positive and equal to ~0.5. Under the test conditions, the kinetic orders were almost independent of temperature and the partial pressures of reactants. The initial copper species (salt or oxide) as a constituent of the catalysts had no effect on the reaction kinetics and mechanism (Table 4; Figs. 1–3); this fact demonstrated the chemical lability of the copper compounds under these conditions [1, 2]. On both of the catalysts, experimental data were described by the exponential equation

$$r = k(P_{CCl_4}P_{O_2})^{0.5}P_{Cl_2}^{0.5}. \qquad (2)$$

The apparent activation energy was 26.3 kcal/mol (Tables 4, 5).

The selectivity of phosgene formation was almost independent of the partial pressure of CCl_4 (experiment

nos. 2, 3, and 5 in Table 5 and nos. 6–8 in Table 4). It mainly depended on the ratio between the partial pressures of oxygen and chlorine in the reaction mixture (Fig. 4). As this ratio was decreased, the selectivity of phosgene formation increased, whereas the overall rate of reaction decreased. On the contrary, an increase in this ratio resulted in an increase in the rate of reaction and the predominant formation of carbon dioxide. An increase in the temperature or the rate of reaction with the use of a more active catalyst (Fig. 4) decreased the selectivity of phosgene formation. This fact suggests the successive conversion of CCl_4 into phosgene and then into CO_2.

Under the test conditions, variations in the P_{O_2}/P_{Cl_2} ratio did not change the chemical and phase composition of molten copper-containing salt systems. These changes were observed only at low P_{Cl_2} [2]. On this basis, the dependence in Fig. 4 can be considered as a consequence of competition between chlorine and oxygen at the active sites of the catalyst. Moreover, currently available data on the structure of salt melts allowed us to formulate a plausible hypothesis concerning the nature of these active sites. Because the adsorption of oxygen at Cu^{2+} ions is impossible [10], it is our opinion that coordinatively unsaturated bivalent copper ions [11, 12], which occur in equilibrium with coordi-
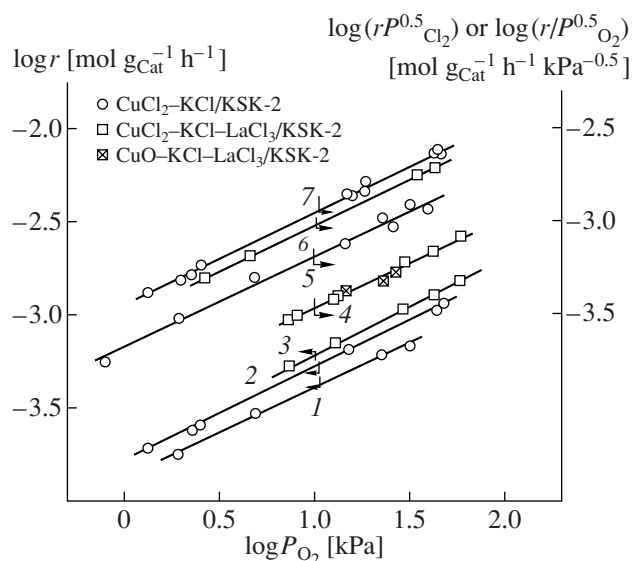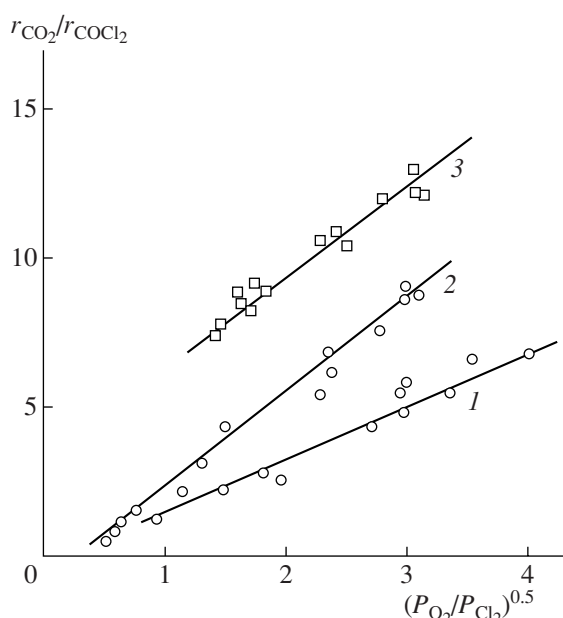
Fig. 3. Kinetic orders of reaction with respect to O_2 on copper-containing salt catalysts at reaction temperatures of (1, 5) 350, (2–4, 7) 375, and (6) 425°C: (1) P_{CCl_4} = 15 and P_{Cl_2} = 3 kPa; (2) P_{CCl_4} = ~9.5 and P_{Cl_2} = 4.8 kPa; (3) P_{CCl_4} = 4 and P_{Cl_2} = 5 kPa; (4) P_{Cl_2} = 4 kPa; (5) P_{CCl_4} = 15 kPa; (6) P_{Cl_2} = 9 kPa; and (7) P_{CCl_4} = ~9 kPa.

Fig. 4. Effect of the ratio between the partial pressures of oxygen and chlorine in the reaction mixture on the ratio between the rates of formation of carbon dioxide and phosgene at (1) 350 and (2, 3) 375°C on the copper–potassium catalyst (1, 2) without and (3) with an additive of $LaCl_3$.

natively saturated $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ ions, can play their role. Under this assumption, the accelerating effect of lanthanum chloride in the catalyst can be explained by the occurrence of lanthanum cations in the outer sphere of coordinatively saturated copper ions. Increased ionic potentials (the charge-to-radius ratios of ions) of such counterions will facilitate a concentration of coordinatively unsaturated ions higher than that in the $CuCl_2$–KCl system.

The independence of reaction order with respect to CCl_4 of the partial pressures of oxygen and chlorine, as well as the independence of reaction orders with respect to O_2 and Cl_2 of P_{CCl_4} (Figs. 1–3), allows us to assume that two types of active sites occur on the catalyst surfaces. Univalent copper cations can be the sites at which the dissociation of CCl_4 occurs. This hypothesis is consistent with the dissociation of CCl_4 at various surface defects of metals and metal oxides [13–16]. Lower valence cations most frequently play the role of defects. This assumption is most consistent with the quantum-chemical characteristics of the molecular structure of CCl_4, which explain the increased electron affinity and dissociation of CCl_4 molecules through the intermediate formation of anions [17]. According to Bell et al. [15], the dissociative adsorption of CCl_4 is characterized by a much greater affinity of the chlorine atom to the metal cation than that in the $\dot{C}Cl_3$ radical.

The laws found, the considerations concerning the nature of active sites, and published data allow us to formulate a simplified two-path reaction scheme for the oxidative dehydrogenation of CCl_4. This reaction scheme includes the steps of the equilibrium dissociative adsorption of initial reactants and chlorine, the conversion of the $\dot{C}Cl_3$ radical into the more stable $\ddot{C}Cl_2$ radical [13, 18], and the oxidation of this latter to phosgene and then to carbon dioxide.

	Stoichiometric coefficients	
	I	II
(1) $2Z + O_2 = 2ZO$	1/2	1
(2) $2Z + Cl_2 = 2ZCl$	0	0
(3) $2Y + CCl_4 = Y\dot{C}Cl_3 + YCl$	1	1
(4) $Y\dot{C}Cl_3 + Z \longrightarrow Y\ddot{C}Cl_2 + ZCl$	1	1
(5) $Y\ddot{C}Cl_2 + ZO \longrightarrow YCOCl_2 + Z$	1	1
(6) $YCOCl_2 = Y + COCl_2$	1	0	(IV)
(7) $YCOCl_2 + ZO \longrightarrow CO_2 + Cl_2 + Y + Z$	0	1
(8) $YCl + ZCl \longrightarrow Cl_2 + Y + Z$	1	1

Reaction path I: $CCl_4 + 1/2O_2 = COCl_2 + Cl_2$

Reaction path II: $CCl_4 + O_2 = CO_2 + 2Cl_2$

Table 4. Rates and rate constants of the oxidative dechlorination of CCl_4 on the (A) $CuCl_2$–KCl–$LaCl_3$ and (B) CuO–KCl–$LaCl_3$ catalysts (1 : 1 : 0.33) supported on KSK-2 with a copper content of 2.8 wt %

Experi- ment no.	Catalyst	T, °C	P_i, kPa					r_i, mol g_{Cat}^{-1} h^{-1}			$k \times 10^6$, mol g_{Cat}^{-1} h^{-1} $kPa^{-0.5}$
			CCl_4	O_2	Cl_2	CO_2	$COCl_2$	CO_2	$COCl_2$	Σ	
1	A	350	4.6	7.7	2.0	1.0	0.20	326	63	389	92
2	A	350	3.7	61.4	4.1	2.0	0.22	677	78	755	102
3*	B	375	0.6	21.3	2.1	0.9	0.07	478	37	515	206
4	B	375	2.0	27.1	4.2	2.1	0.20	660	61	721	202
5	B	375	16.0	14.6	4.1	2.2	0.19	1488	155	1643	219
6*	A	375	1.5	20.6	6.1	0.8	0.10	432	48	480	217
7	A	375	18.0	16.8	6.2	2.9	0.31	1366	160	1526	218
8	A	375	23.8	16.9	6.4	3.3	0.45	1611	172	1783	225
9	A	375	4.7	41.6	5.4	2.9	0.33	1168	97	1265	211
10	A	375	4.0	57.3	6.1	3.0	0.24	1230	100	1330	215
11	A	400	14.5	12.2	7.7	3.8	0.40	1750	190	1940	406
12	A	425	3.7	4.5	9.4	4.6	0.71	1045	161	1206	912
13	A	425	1.8	41.6	8.9	4.3	0.21	2473	122	2595	900

* Experiments with the additional introduction of chlorine into the reaction zone.

Table 5. Rates and rate constants of the oxidative dechlorination of CCl_4 on the $CuCl_2$–KCl catalyst (1 : 1) supported on KSK with a copper content of ~7 wt %

Experi- ment no.	T, °C	P_i, kPa					r_i, mol g_{Cat}^{-1} h^{-1}			$k \times 10^6$, mol g_{Cat}^{-1} h^{-1} $kPa^{-0.5}$
		CCl_4	O_2	Cl_2	CO_2	$COCl_2$	CO_2	$COCl_2$	Σ	
1	325	17.8	22.5	1.57	0.74	0.36	237	74	311	19.5
2*	350	1.0	16.9	4.53	0.14	0.06	67	27	94	48.9
3*	350	1.9	17.3	5.7	0.19	0.08	83	36	119	49.6
4	350	10.0	14.5	1.83	0.92	0.21	374	87	461	51.8
5*	350	12.4	16.2	5.04	0.44	0.15	220	77	297	47.0
6	350	12.2	39.6	3.14	1.46	0.22	493	74	567	45.7
7*	375	11.6	2.2	4.95	0.34	0.31	139	125	264	116
8	375	8.5	15.1	3.05	1.47	0.27	650	121	771	119
9*	375	8.8	18.4	11.2	0.84	0.26	323	103	426	112
10	375	9.1	45.0	5.10	2.53	0.28	968	108	1076	120
11	400	7.9	12.1	4.56	2.25	0.31	973	134	1107	242

* Experiments with additional introduction of chlorine into the reaction zone.

Reaction scheme (IV) implies the occurrence of two types of active sites: Z (coordinatively unsaturated ions of bivalent copper) and Y (univalent copper ions).

As a result of this study, we found the rate laws and proposed a mechanism of the reaction. However, they should be tested experimentally under conditions of the oxidative chlorination of methane. Under these conditions at minimum partial pressures of Cl_2 in the reaction mixture, changes in the chemical and phase compositions of the catalysts and their catalytic properties can occur [2].

REFERENCES

1. Aglulin, A.G., *Kinet. Katal.*, 1995, vol. 36, no. 5, p. 702.

2. Aglulin, A.G., *Kinet. Katal.*, 1995, vol. 36, no. 5, p. 709.

3. Temkin, M.I., Kiperman, S.L., and Luk'yanova, L.I., *Dokl. Akad. Nauk SSSR*, 1950, vol. 74, no. 4, p. 763.

4. Lur'e, A.A., *Sorbenty i khromatograficheskie nositeli (spravochnik)* (Sorbents and Chromatographic Supports: A Handbook), Moscow: Khimiya, 1972.

5. USSR Inventor's Certificate no. 845 050, *Byull. Izobret.*, 1981, no. 25.

6. Yamada, J. and Kanetaki, S., *Jpn. Kokai Tokkyo Koho*, 1979, vol. 79, p. 139.

7. Machkarovskaya, I.A., Burshtein, K.Ya., and Petrosyan, V.A., *Izv. Akad. Nauk, Ser. Khim.*, 1995, no. 11, p. 2155.

8. Denisevich, E.V. and Tesner, P.A., *Neftekhimiya*, 1981, vol. 21, no. 4, p. 552.

9. Kurlyandskaya, I.I., Bakshi, Yu.M., Kudryavtseva, T.F., Dmitrieva, M.P., and Gel'bshtein, A.I., *Kinet. Katal.*, 1984, vol. 25, no. 3, p. 598.

10. Allen, J.A. and Clark, A.J., *J. Appl. Chem.*, 1966, vol. 16, p. 327.

11. Volkov, S.V., *Ionnye rasplavy* (Ionic Melts), Kiev: Naukova Dumka, 1975.

12. Volkov, S.V., Grishchenko, V.F., and Delimarskii, Yu.K., *Koordinatsionnaya khimiya solevykh rasplavov* (Coordination Chemistry of Salt Melts), Kiev: Naukova Dumka, 1977.

13. Stenkowsky, V.S., Cheng, C.C., and Yates, Jr.J.T., *Surf. Sci.*, 1989, vol. 215, nos. 1–2, p. L279.

14. Stenkowsky, V.S. and Yates, J.T., Jr., *Surf. Sci.*, 1990, vol. 232, nos. 1–2, p. 102.

15. Bell, R.C., Zemski, K.A., and Castleman, A.W., *J. Phys. Chem. A*, 1999, vol. 103, no. 11, p. 1585.

16. Mink, G., Bertoti, I., and Szekely, T., *React. Kinet. Catal. Lett.*, 1985, vol. 27, no. 1, p. 39.

17. Timokhin, B.V., *Usp. Khim.*, 1990, vol. 59, no. 2, p. 332.

18. Michael, J.V. and Lim, K.P., *J. Phys. Chem.*, 1993, vol. 97, no. 9, p. 1914.