Effect of the Composition of Supported Copper-Containing Salt Catalysts on Their Activity in the Deacon Reaction: Dependence of the Rate of the Deacon Reaction on the Ratio between Copper and Potassium Chlorides in a Supported CuCl₂-KCl Salt Catalyst

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Abstract—The effect of KCl/CuCl₂ molar ratios from 0 to 2.5 in the CuCl₂–KCl catalyst (support) on its activity in the Deacon reaction was studied by a gradientless method in a temperature range of $350-425^{\circ}$ C. The essential role of the hydration processes of the salt catalyst components in the homogenization of a reaction layer was established. The experiments did not contradict the previously proposed reaction kinetics and mechanism. A possible explanation of the experimental results was given based on the polarization representations used earlier in the reaction mechanism.

Keywords: Deacon reaction, supported catalyst, copper chloride, molar ratio between components, reaction rate **DOI:** 10.1134/S0023158419030017

INTRODUCTION

The reaction of hydrogen chloride oxidation to molecular chlorine (the Deacon reaction)

$$4HCl + O_2 = 2Cl_2 + 2H_2O$$
 (I)

remains of considerable current interest primarily because of the promising possibility of obtaining cheap chlorine from abgas hydrogen chloride. The most popular catalysts of this reaction are coppercontaining salt compositions in a supported form or in the form of melts [1-6]. In addition, this reaction forms a basis for the oxidative chlorination of aliphatic hydrocarbons, for example, methane [7-9]:

$$CH_4 + nHCl + 0.5nO_2 = CH_{4-n}Cl_n + nH_2O.$$
 (II)

The appearance of alternative catalysts (which were considered previously [9], for example, [10, 11]) did not diminish interest in traditional copper-containing salt catalysts due to the lack of real achievements in these two reactions.

In previous studies, the effect of the composition of copper-containing catalysts on their activity in the Deacon reaction has been little examined. The available information is limited and controversial even for the supported $CuCl_2$ -KCl binary catalyst. Thus, according to a pioneering study by Shakhovtseva et al. [4], the rate constant of reaction (I) is an extremal

function of the molar ratio between potassium and copper chlorides with a maximum close to 0.1. According to Bakshi and Aglulin [12], the reaction activity maximum corresponds to the composition with a ratio between these components close to 0.5. However, according to Gel'bshtein and Bakshi [13], the activity maximum belongs to the equimolar amounts of potassium and copper chlorides in the catalyst (KCl/CuCl₂ = 1). The same result was obtained by Garcia and Resasco [7] but under the conditions of reaction (II).

The aim of this extended study was to clarify this controversial issue. It was also of interest to compare its results with new ideas about the mechanism of the Deacon reaction [9].

EXPERIMENTAL

The effect of the molar ratio KCl/CuCl₂ between chlorides in a range from 0 to 2.5 in the catalyst on the rate of HCl oxidation was studied using a gradientless flow-circulation method [14, 15] at atmospheric pressure in a temperature range of 350–425°C. The preparation of supported catalysts and their analysis for copper content were similar to those described previously [9]. Diatomite DN-2 ($S_{sp} \approx 1-1.5 \text{ m}^2/\text{g}$) and silica gel KSK ($S_{sp} \approx 340 \text{ m}^2/\text{g}$) both with a grain size of 0.25– 0.5 mm were used as supports [9]. As was shown previously [4], the use of this particle size under the con-

[†] Deceased.

ditions of the Deacon reaction excludes the effect of internal diffusion in a catalyst granule at temperatures of $350-425^{\circ}$ C. In the prepared catalyst with a ~25 wt % concentration of catalytic salts (6.7 wt % Cu), the surface of diatomite is almost completely covered with salt melt. In a silica gel catalyst of the same composition, the surface areas of the salt melt and the surface free of melt are 180 and 170 m²/g, respectively [16–18]. As was found by Zurowski [19] and established in this work, silica gel is inert in the reaction of HCl oxidation.

Currently, there is no doubt that the oxidation of HCl can occur in the volume of a copper-containing salt melt dispersed on a support. However, the experimental evaluation of the specific rates of reaction (I) at different ratios between the components in the catalyst seems impracticable due to the possibility of incomplete partial melting of copper chloride [20]. As judged from phase diagrams [21, 22], the phase heterogeneity of a copper-containing salt system and a change in the composition of its active part in the melt are inevitable. At certain ratios between the salt components, their precipitation as solid phases from the melt was detected. For example, at K/Cu = 0.1, copper chloride should be such a component. In the case of K/Cu = 0, i.e., on solid copper chloride ($T_{\rm m} = 596^{\circ}$ C) without modifiers, the reaction zone is most likely limited to its surface area. Therefore, with consideration for the data of phase thermal analysis, it is believed that copper-containing salt catalysts for the Deacon reaction are only partial melts in some cases [20].

Experiments with different ratios between salt components in the catalysts were carried out taking into account their possible features. To obtain the true specific rates of the reaction, it was necessary to determine the conditions under which the entire volume of the salt catalyst and all of its active centers participate in the reaction. For this purpose, a technique tested earlier [9] was used for comparing reaction rates on catalysts with different salt film thicknesses on a support. This was achieved either by changing the total amount of salts of the same composition on the support or by a significant change in the specific surface area of the support in the catalyst. The replacement of diatomite DN-2 by silica gel KSK-2 decreased the average salt film thickness of the catalyst by more than an order of magnitude at the same salt content [16, 17]. In accordance with this procedure, it was possible to observe [9] a constant reaction rate constant at substantially different thicknesses of salt films with an equimolar ratio between copper and potassium chlorides. This experimental fact was a basis for the conclusion that the entire volume of the molten salts participated in the reaction and the active sites of this catalyst were available to the reactants.

As previously [9], the experiments were carried out far from equilibrium under the conditions of a zero order with respect to hydrogen chloride. This circumstance facilitated the identification of the kinetic regularities of the reaction on different catalysts and, under these conditions, almost excluded possible changes in their phase and chemical compositions under the influence of a reaction atmosphere. No reaction products (chlorine and water vapor) were added to the initial mixture. Therefore, in accordance with the stoichiometry of the equation of reaction (I), their concentrations were the same in all of the experiments.

In order to avoid distortions in a ratio between the chlorides in catalysts and in apparent reaction rates due to the volatility of copper chlorides at temperatures of 400 and 425°C, the experiments were carried out for a limited time as described previously [9].

RESULTS AND DISCUSSION

The study of the influence of the partial pressure of hydrogen chloride in the reaction mixture (P_{HCl}) on the rate of its oxidation (r_{HCl}) at the almost constant levels of P_{O_2} and P_{Cl_2} showed that the dependence of r_{HCl} on P_{HCl} (including similar experiments with an equimolar ratio between copper and potassium chlorides [9]) is independent of the ratio between compo-

nents in the catalyst. In all cases, the value of $P_{\text{HCI}}^{\text{min}}$, below that the rate of HCl oxidation began to decrease remained at approximately the same level of ~4 kPa (Fig. 1). It is reasonable to believe that the thermal decomposition of copper chloride in catalysts is accompanied by its rapid regeneration due to the stages of the interaction of copper chloride and copper oxychloride with oxygen and HCl under the conditions of a zero-order reaction with respect to hydrogen chloride (regardless of the K/Cu ratio). Therefore, only minimal concentrations of the intermediate forms of copper compounds in the composition of catalysts would be expected under these conditions. As

was shown previously [9], at $P_{\rm HCl} < P_{\rm HCl}^{\rm min}$, the stationary composition of the catalyst and the reaction kinetics changed with the formation of oxygen-containing copper compounds because of an imbalance in the rates of the main stages.

Taking into account the observed chemical similarity of the test catalysts, let us assume that (as with an equimolar ratio between potassium and copper chlorides [9]) the kinetic order of the reaction with respect to chlorine under the conditions of a zero order with respect to hydrogen chloride is -0.65. The plausibility of this index of reaction inhibition by chlorine was confirmed by the kinetic order with respect to oxygen, which is close to ~ 0.75 (as reported previously [9]) regardless of the composition of the catalyst (Fig. 2).

The corresponding equation

$$r = k_1 P_{\rm O_2}^{0.75} / P_{\rm Cl_2}^{0.65} \tag{1}$$

was found consistent with the experimental data (Table 1). A change in the KCl/CuCl₂ ratio in catalysts from 0.1 to 0.5 did almost not affect the apparent acti-



Fig. 1. Dependence of the rates of HCl oxidation (*r*) on P_{HCl} on supported copper–potassium catalysts at 375°C in (*I*-3) the Deacon reaction and (4) methane oxychlorination at different molar ratios between the salt components: (*I*) K/Cu = 1.5 ($P_{\text{O}_2} = 12 \text{ kPa}$, $P_{\text{Cl}_2} = 1.3 \text{ kPa}$), (2) K/Cu = 0.1 ($P_{\text{O}_2} = 10 \text{ kPa}$, $P_{\text{Cl}_2} = 3 \text{ kPa}$), (3) K/Cu = 0.5 ($P_{\text{O}_2} = 12 \text{ kPa}$, $P_{\text{Cl}_2} = 1.0 \text{ (}P_{\text{O}_2} = 11 \text{ kPa}$, $P_{\text{Cl}_2} = 0.7 \text{ kPa}$, and $P_{\text{CH}_4} = 48 \text{ kPa}$). In all cases, the quantity P_{Cl_2} characterizes the region of a zero order of the reaction with respect to hydrogen chloride.

vation energy (36–38 kcal/mol). The results of the kinetic study do not contradict the concept of the two-route mechanism of reaction (I) proposed earlier [9].

In the experiments performed on the CuCl₂/support catalyst in the complete absence of potassium chloride (Table 2), based on the mechanism of reaction (I) [9], it is possible to exclude the route of HCl oxidation with the participation of coordinatively unsaturated active centers in the complex $CuCl_4^{2-}$. Therefore, reaction (I) on this catalyst should occur along only one route, and the following equation can be used for its analysis:

$$r = k_2 P_{\rm O_2} / P_{\rm Cl_2}.$$
 (2)

Thus, the found increased value of the activation energy of the reaction (~59 kcal/mol) illustrates the role of an activator, which is potassium chloride in this case, in the salt catalyst. The presence of potassium ions in the outer sphere of the complex CuCl_4^{2-} —the active center of reaction (I)—leads to the appearance of coordinatively unsaturated analogs of CuCl_4^{2-} and the weakening of bonds in it.

The experiments with varying the salt film thickness of the catalysts by the two methods described in the Experimental section at K/Cu ratios from 0.1 to



Fig. 2. Kinetic orders of the Deacon reaction with respect to oxygen on a copper–potassium salt catalyst at different molar ratios between the components: $\text{KCl/CuCl}_2 = 0.1$, (1) 375°C and (4) 400°C; $\text{KCl/CuCl}_2 = 0.25$, (5) 400°C; $\text{KCl/CuCl}_2 = 0.5$, (3) 375°C; and $\text{KCl/CuCl}_2 = 1.5$, (2) 400°C.

1.5 (Table 1) showed unchanged constants of Eq. (1) within the limits of each particular composition. This fact makes it possible to state the participation of all active sites present in the volume of each catalyst in the reaction regardless of the ratio between the salt components. In particular, note that this conclusion can be extended to compositions with obvious phase heterogeneity (for example, at K/Cu = 0.1 (Table 1, experiment nos. 2–7)) and even to the catalyst based on solid copper chloride (K/Cu = 0). As can be seen, a sharp increase in the surface area of the supported copper chloride by replacing diatomite with silica gel (Table 2, experiment nos. 1–6) did not change the rate constant of the reaction per gram of copper in the catalyst.

Thus, it can be argued that, under the conditions of zero-order reaction with respect to hydrogen chloride, supported copper-containing salt catalysts of different composition exhibit the properties of homogeneous melts dispersed on the supports. Because of this, their initial phase heterogeneity in some cases does not prevent the participation of all potentially active sites available in the reaction layer of the catalysts in the reaction. On this basis, in my opinion, the long-established idea [20] that copper-containing salt catalysts are partial melts under reaction conditions is erroneous on condition of the absence of diffusion limitations for reactants in the bulk of the salt melt.

The unexpected facts obtained can be explained if we take them as direct evidence for a significant role of the hydration processes of salt catalyst components under the conditions of the Deacon reaction. This is

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Experi-	Support	Cu, wt %	<i>T</i> , °C →		<i>P_i</i> , kPa		$r_{\rm HCl} \times 10^4$,	$k_1 \times 10^4$,					
ment				O ₂	HCl	Cl ₂	$\mathrm{mol}_{\mathrm{HCl}}\mathrm{g}_{\mathrm{Cu}}^{-1}\mathrm{h}^{-1}$	$mol_{HCl} g_{Cu}^{-1} h^{-1} kPa^{-0.1}$					
Molar ratio $KCl/CuCl_2 = 0.1$													
1	KSK-2	11.2	350	20.3	17.8	1.42	214	28.1					
2	DN-2	1.35	375	11.0	11.5	1.85	392	96.8					
3		3.57		11.5	10.2	1.45	455	92.5					
4		6.7		9.8	9.7	1.53	437	104					
5		8.9		10.0	12.6	1.40	408	90.3					
6	KSK-2	9.6	375	10.3	10.3	1.46	416	92.5					
7		10.9		32.4	17.6	3.53	522	87.3					
8	DN-2	9.3	400	48.9	11.55	5.65	1790	298					
Molar ratio $KCl/CuCl_2 = 0.25$													
9	DN-2	8.9	350	12.7	8.7	1.44	282	54.5					
10		8.9	375	12.1	11.6	3.13	613	198					
11		8.7	400	12.3	11.4	6.16	1193	592					
12		8.8	425	12.2	10.2	9.77	2340	1577					
Molar ratio $\text{KCl/CuCl}_2 = 0.5$													
13	KSK-2	8.8	350	20.2	17.1	2.22	450	79					
14		8.8	375	12.5	15.4	4.18	705	269					
15		9.1	400	12.1	9.4	7.34	1420	800					
16	DN-2	8.9	400	4.6	14.6	4.43	902	756					
17	KSK-2	9.3	400	19.8	11.3	9.50	1770	813					
18		9.3	425	8.4	13.2	11.01	2390	2320					
				Molar ra	atio KCl/C	$uCl_2 = 1.0$							
19	DN-2	6.7	350	9.3	9.5	0.93	312	55.9					
20			375	44.9	9.0	3.78	1240	171					
21			400	32.1	12.7	5.06	1730	368					
22			415	10.0	6.0	4.25	1440	656					
				Molar ra	atio KCl/C	$uCl_2 = 1.5$							
23	KSK-2	6.6	350	21.3	18.9	0.83	217	19.4					
24		6.4	375	19.4	19.1	1.28	350	44.5					
25		6.2	400	28.9	18.1	3.40	675	120					
26		6.1	425	15.4	20.1	4.40	875	295					
27		6.0	450	13.6	26.45	6.09	1064	486					
28	DN-2	5.85	400	43.4	12.4	3.14	955	119					
Molar ratio $KCl/CuCl_2 = 2.5$													
29	DN-2	4.4	375	22.2	11.7	0.52	159	10.2					
30		4.3	400	34.3	17.6	1.03	345	24.8					

Table 1. Rates (*r*) and constants of Eq. (1) for the rate of HCl oxidation (k_1) on a supported copper-potassium catalyst at different temperatures and KCl/CuCl₂ molar ratios

Entry	Support	Cu, wt %	T, ℃		P_i , kPa		$r_{\rm HCl} \times 10^4$,	$k_2 \times 10^4$,
				O ₂	HCl	Cl ₂	$\mathrm{mol}_{\mathrm{HCl}}\mathrm{g}_{\mathrm{Cu}}^{-1}\mathrm{h}^{-1}$	$\mathrm{mol}_{\mathrm{HCl}}\mathrm{g}_{\mathrm{Cu}}^{-1}\mathrm{h}^{-1}$
1	DN-2	9.9		45.4	11.0	0.73	112	1.80
2				22.3	10.9	0.46	87	1.79
3	KSK-2	11.5		20.3	20.8	0.51	75	1.88
4		11.4	350	36.6	15.6	0.67	95	1.74
5	DN-2	9.0		40.5	23.1	0.54	133	1.83
6		9.2		15.9	23.7	0.38	75	1.80
7		9.8	375	27.5	34.6	1.40	297	15.1
8		8.6	400	23.2	33.5	3.36	581	84.3
9		8.4	425	18.3	25.8	6.20	1210	410

Table 2. Rates (r) and constants of Eq. (2) for the rate of HCl oxidation (k_2) on a CuCl₂/support catalyst

supported by the ability of alkaline cations [22–25] and chloride anions [25] to undergo hydration and their stability in this form over a wide temperature range. The atoms and ions of transition metals and lanthanides also exhibit a tendency to hydration. The model of a short-range order in a concentrated aqueous solution of lanthanum chloride proposed by Grigoriew and Siekierski [26] based on X-ray diffraction analysis data can serve as an example; they considered this solution like a hydrated salt melt because it did not contain free water.

It is likely that the hydration of salt catalysts in the course of the reaction is a major factor in their homogenization. The estimates of the specific rates of the reaction (Table 1) obtained in the absence of diffusion limitations from the reaction layers of the catalysts made it possible to reliably judge the effect of a ratio between the salts on their activity in the reaction. The applicability of Eq. (1) to these experiments, with the exception of the case with K/Cu = 0, suggests that the two-route mechanism proposed previously [9] for the oxidation of HCl remained unchanged regardless of a ratio between the components in the catalyst. In accordance with this mechanism, the polarizing action of outer-sphere potassium ions should lead to an acceleration of the reaction due to the weakening of bonds in the internal coordination sphere of the complex $CuCl_4^{2-}$ and the formation of its coordinatively saturated analogs—the active centers of the second

saturated analogs—the active centers of the second route. On this basis, an increase in the specific activity of the catalyst with increasing the KCl/CuCl₂ ratio in it would be expected. However, in practice, these expectations were only partially met when this ratio was changed from 0.1 to 0.5 regardless of temperature (Fig. 3). Contrary to the expectations, with a further increase in the K/Cu ratio in the composition of the catalyst, the constant of Eq. (1) clearly decreased at a slightly reduced but stable level of activation energy (32–33 kcal/mol).

The constant kinetics and, apparently, mechanism of the reaction and the full participation of all available active centers in each particular case suggest that the number of these centers in the catalysts decreased with the KCl/CuCl₂ ratio in them. In my opinion, a natural reason for this trend can be the interaction of potassium chloride with copper chloride as a supplier of

 Cu^{2+} ions, which occur in the complex form $CuCl_4^{2-}$ in the melt [27]. According to Zurowski [19], the reaction of these salts proceeds easily with the formation of



Fig. 3. Effect of the molar ratio KCl/CuCl₂ in a copper– potassium catalyst under conditions of a zero-order reaction with respect to hydrogen chloride on the apparent rate constant of the Deacon reaction at temperatures of (1) 350, (2) 375, and (3) 400°C.

the unstable compound K_2CuCl_4 , which decomposes into inert KCl and KCuCl₃.

Thus, although the formation of the double salt KCuCl₃ in some cases facilitates the transfer of copper-containing salts into the melt at lower temperatures and increases their stability, in my opinion, it simultaneously decreases the catalyst activity in the reaction with increasing the K/Cu ratio. On this basis, it can be argued that the curves shown in Fig. 3 were obtained without taking into account a possible significant change in the stationary concentration of an active copper species under the reaction conditions with changes in the ratio between the salts in the catalyst. To obtain plausible information on the effect of the ratio between the chlorides on the catalyst activity, it is necessary to maintain a constant concentration of the active form of copper in such experiments. It is obvious that corresponding adjustments are relevant because they can fundamentally change the shape of curves in Fig. 3. This problem can be solved only by controlling the concentration of the active form of copper in the catalysts (for example, based on the known kinetics of formation of KCuCl₃ under the reaction conditions or by other methods). However, rough estimates can be made by comparing the results of experiments conducted on catalysts with significantly different ratios between the components with consideration for the easy interaction of copper and potassium chlorides [29].

The essence of this approximate approach can be understood if we compare, for example, experiment nos. 10 and 24 (Table 1) at a temperature of 375°C on the catalysts with chloride ratios of 0.25 and 1.5, which, in my opinion, are known to differ in the levels of active copper losses in them. In experiment no. 10, it is reasonable to tentatively accept a minimal level of losses and the constant of Eq. (1) $(k_1 = 198 \times 10^{-4} \text{ mol}_{\text{HCl}} \text{ g}^{-1}_{\text{Cu}} \text{ h}^{-1} \text{ kPa}^{-0.1})$ almost undistorted, which is not the case in experiment no. 24 with the apparent constant $k_1 = 44.5 \times$ $10^{-4} \operatorname{mol}_{HCl} g^{-1}{}_{Cu} h^{-1} kPa^{-0.1}$. If we assume that ~90% of the active copper under the conditions of this experiment could not appear due to an increased rate of CuCl₂ conversion into KCuCl₃ (which is quite realistic due to the ease of its formation [15] and an increased concentration of potassium chloride), a corresponding correction leads to a new estimate of the constant of Eq. (1) $k_1 \approx 400 \times 10^{-4} \text{ mol}_{\text{HCl}} \text{ g}^{-1}_{\text{Cu}} \text{ h}^{-1} \text{ kPa}^{-0.1}$. Such semiquantitative corrections with consideration for temperature and the effect of chloride concentration in the catalysts finally led with a similar result to a constant increase in the catalyst activity with increasing the KCl/CuCl₂ ratio instead of a decrease. This fact gives reasons for considering an essential role of polarization interactions in the Deacon reaction mechanism [9] over the entire range of ratios between the components of a copper-potassium salt catalyst. Nevertheless, additional information is required in order to confirm this conclusion.

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