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Oxidative Chlorination of Aliphatic Hydrocarbons and Their Chloro-derivatives

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The problems of the thermodynamics, the selection of catalysts, and the kinetics and mechanisms of the oxidative chlorination reactions of aliphatic hydrocarbons and their chloro-derivatives and the technological arrangement in the reactor unit are considered in relation to C_1-C_3 hydrocarbons.
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I. INTRODUCTION

Oxidative chlorination (or oxychlorination) is the hydrocarbon chlorination reaction occurring with participation of an oxidising agent, which is usually oxygen. The chlorinating agent is as a rule hydrogen chloride, the need to use large amounts of which has in fact been the cause of the development of the oxychlorination method.

The oxychlorination of a wide range of hydrocarbons and their chloro-derivatives has been described in the literature. The oxychlorination is carried out in the gas phase in the presence of a heterogeneous catalyst and also in the melt and in a catalyst solution.[1-5] Since it is most widely used, attention is concentrated in the review on the first of the above procedures. A number of studies have been devoted to oxychlorination in salt melts,[6-9] while oxychlorination in solutions of catalytically active salts has been described in detail in recently published reviews[10,11] and dissertations.[12,13]

Many publications have been devoted to the gas-phase heterogeneous-catalytic oxychlorination of hydrocarbons and their chloro-derivatives, covering many aspects of this problem[14,15] or its individual aspects, such as the selection of catalysts and the mechanism of their action,[16,17] the kinetics and mechanisms of the reactions,[18] the relevant technology and economics, and a review of the patent literature.[19,20]

The present article is devoted to the consideration of the current state of the problems of the thermodynamics, the selection of catalysts, and the kinetics and mechanisms of the oxychlorination reactions as well as the technological arrangement for the processes, mainly in relation to C_1-C_3 hydrocarbons and their chloro-derivatives, since the fundamental questions of theory and practice have been dealt with in studies on the oxychlorination of these compounds.

In terms of the mechanism, all the oxychlorination reactions can be subdivided into two large groups: (1) reactions which proceed via the intermediate oxidation of hydrogen chloride by oxygen to chlorine, which chlorinates the organic substrate; (2) reactions which do not require the preliminary oxidation of hydrogen chloride to chlorine. The substitutional oxychlorination reactions of alkanes (and chloroalkanes) belong mainly to the first group, whilst the second group includes the additive oxychlorination reactions of alkenes (and chloroalkenes):

$$2HCl + 0.5O_2 \rightleftarrows Cl_2 + H_2O,$$

$$RH + Cl_2 \rightarrow RCl + HCl,$$

$$>C=C< + 2HCl + 0{,}5O_2 \rightarrow >\underset{Cl}{C}-\underset{Cl}{C}< + H_2O \quad .$$

Gel'bshtein[18] placed the chlorination of alkenes in a separate group:

$$>C=C<_{H} + HCl + 0.5O_2 \rightarrow >C=C<_{Cl} + H_2O \quad .$$

The reaction takes place at temperatures at which hydrogen chloride is oxidised and alkanes undergo substitutional oxychlorination, but there is no chlorine in the gas phase. It may be that the reaction proceeds via additive oxychlorination with subsequent dehydrochlorination. The elimination of hydrogen chloride is observed in high-temperature oxychlorination.[13] The additive oxychlorination of alkenes occurs at temperatures up to 300 °C (there is virtually no oxidation of hydrogen chloride to chlorine under these conditions), while the substitution oxychlorination of alkenes and alkanes takes place at temperatures above 350 °C.[1,14,15]

Processes involving the oxidative chlorination of ethylene to dichloroethane[1,14,20] and of ethylene, propene, and their chloro-derivatives to carbon tetrachloride, trichloroethylene, and tetrachloroethylene[21,22] have found extensive industrial application. The development of an oxychlorination technology in melts of metal chlorides and oxide chlorides has also been reported,[23,24] but there has been no information about its practical exploitation, which indicates difficulties in the industrial application of such a process.

We shall consider the individual aspects of the oxychlorination reactions.

II. THERMODYNAMICS

The reversible oxidation reaction of hydrogen chloride (the Deacon reaction) is of greatest interest from the thermodynamic point of view. The problems concerning the thermodynamics of this reaction have been examined in fair detail in earlier reviews.[1,14] The constants K_p and the degrees of conversion of HCl and O_2 decrease appreciably with increase in temperature. According to Arnold and

Kobe's data,[25] the following expression relating lg K_p to temperature is valid in the temperature range 200–2000 °C: lg K_p = 5881.7/T–0.93035 lg T + 1.3704 × 10^{-4} T–1.758 × 10^{-8} T^2–4.1744, or in a simplified form: lg K_p = 6104.0/T–7.0994. When the Deacon reaction and the chlorination reaction take place simultaneously, the reaction equilibrium shifts as a result of the consumption of chlorine, which may entail the virtually complete conversion of hydrogen chloride.[1]

III. CATALYSTS

Numerous studies have been devoted to the selection of new and the improvement of existing catalytic oxychlorination systems.[1,14,15] They concern the question of the choice of the most active and selective catalytic compositions, carriers, and methods for the preparation of catalysts and the stabilisation of their operation. Despite a number of advances achieved on these lines, copper(II) chloride, proposed as the catalyst for the oxidation of hydrogen chloride as early as the XIXth century, still remains the main constituent of the catalysts for the Deacon and oxychlorination reactions.

It is most likely that hydrogen chloride is oxidised in accordance with Scheme 1, which includes copper reduction and oxidation stages:[26,29]

Scheme 1

$$2CuCl_2 \rightleftarrows Cu_2Cl_2 + Cl_2 \text{ (gas)},$$
$$Cu_2Cl_2 + 0.5O_2\text{(gas)} \rightleftarrows CuO \cdot CuCl_2,$$
$$CuO \cdot CuCl_2 + 2HCl \text{ (gas)} \rightleftarrows 2CuCl_2 + H_2O \text{ (gas)}.$$

It has been suggested[27] that a peroxy-compound is formed in the reaction with oxygen in order to account for the observed second-order of the reaction with respect to copper monochloride:

$$2CuCl_2 \rightleftarrows 2CuCl + Cl_2 \text{ (fast)},$$
$$2CuCl + O_2 \rightarrow Cu_2O_2Cl_2 \text{ (slow)},$$
$$Cu_2O_2Cl_2 + 4HCl \rightarrow 2CuCl_2 + Cl_2 + 2H_2O .$$

The direct interaction of bivalent copper chloride with oxygen is unlikely in view of the positive value of ΔG for this reaction.[18,26-29]

Gel'bshtein and co-workers[30-32] did not consider the decomposition of bivalent copper chloride with evolution of chlorine, assuming that chlorine is evolved in two steps: in the adsorption of oxygen and in its subsequent interaction with the adsorbed hydrogen chloride (Scheme 2):

Scheme 2

$$[Cu_mCl_n] + 2HCl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Cu_mCl_n \cdot 2HCl] \text{ (slow)},$$
$$[Cu_mCl_n \cdot 2HCl] + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [Cu_mCl_n \cdot 2HCl \cdot O_2] \text{ (slow)},$$
$$[Cu_mCl_n \cdot 2HCl \cdot O_2] + 2HCl \overset{k_3}{\rightleftarrows} [Cu_mCl_n] + Cl_2 + 2H_2O \text{ (fast)},$$
$$[Cu_mCl_n \cdot 2HCl] + Cl_2 \overset{k_4}{\rightleftarrows} [Cu_mCl_n \cdot 2HCl \cdot Cl_2] \text{ (fast)}.$$

One of the causes of the high catalytic activity of copper is its capacity for complex formation. It has been assumed that the interaction with oxygen does not go as far as the formation of copper oxide chloride but stops at the chemisorption stage. The oxidation reduction transformation of the copper cation in the Deacon reaction then proceeds in one stage – chloride ions transfer electrons to the absorbed oxygen via the copper cations, i.e. via a relay mechanism. Nevertheless, in the latest studies by the same workers[18,33] preference was given to the mechanism postulating the decomposition of $CuCl_2$ with evolution of chlorine.

The formation of univalent copper in catalytic systems has been established by the majority of investigators[26-29,33,34] and in many studies[26-29,33] the stages of Scheme 1 were investigated separately. Scheme 1 can serve as a good illustration of one of the first theories of catalysis, which explains the mechanism of the catalytic action by the formation of intermediate compounds, which are then converted into the reaction products with regeneration of the initial catalyst.

According to a series of data,[31,32,35-37] the first stage of the oxychlorination reaction of hydrocarbons, namely the oxidation of hydrogen chloride to chlorine, takes place at the same rate in the presence and absence of the hydrocarbon. Since the subsequent chlorination can proceed also without the participation of the catalyst, the main task in the development of a catalytic system for these reactions is the selection of the active component for the first stage.

Systems consisting of a carrier impregnated with copper chlorides and added chlorides of alkali, alkaline earth, lanthanide, and more rarely, other elements are most widely used as catalysts for the oxychlorination of methane.[38,39] A catalyst based on chromium oxide is also frequently employed.[40] An attempt has been made to combine the two familiar catalysts in the structure of the copper-chromium spinel $CuCr_2O_4$.[41,42] Catalysts based on iron[43] and its mixtures with copper, chromium, and alkali metals have also been described.[44] Rarer catalytic systems are also used: platinum, ruthenium, and potassium complexes on a carrier[45] and a mixture of palladium and lithium chlorides with added calcium, sodium, and potassium chlorides.[46]

The activities of the basic catalysts for the oxychlorination of methane enumerated above have been compared[42] and it has been shown that the most active catalyst is copper(II) chloride mixed with potassium and lanthanide chlorides. The attempts to bind copper in the spinel structure ($CuAl_2O_4$, $CuCr_2O_4$) and to use involatile copper compounds (CuF_2) were unsuccessful, since, under the conditions of an excess of hydrogen chloride and an elevated temperature, all these compounds are gradually converted into copper(II) chlorides.

It has been suggested[47] that copper be used in the form of the oxide, sulphate, nitrate, phosphate, stannate, plumbate, chromate, molybdate, vanadate, etc. in a mixture with compounds of the lanthanide elements. However, under oxychlorination conditions one may expect their gradual conversion into chlorides, so that the real catalytic system would not then differ from the traditional one.

Communications concerning the possibility of the oxychlorination of methane at relatively low temperatures (less than 200 °C) by using colloidal silicon dioxide as the carrier have appeared recently.[48-50] A salt melt without a carrier is frequently used for the oxychlorination of methane.[8,9,23,24,26]

It has been shown[15] that catalysts for the oxidative chlorination of ethane hardly differ from the systems used for the oxychlorination of methane.

Under the oxychlorination conditions, the mixture of the chlorides of copper, alkali metals, and a number of promoting agents is present as a rule on the carrier surface in the molten state.[1,14,15,30,35,51] It is noteworthy that the appearance of univalent copper in the system as well as the introduction into the latter of alkali metal chlorides reduces the melting point of the eutectic. This results in the formation of complexes having different chemical compositions[26-52] – $KCuCl_3$, K_2CuCl_4, K_2CuCl_3, and $K_2Cu_2Cl_6$. Lanthanide metal chlorides also greatly lower the melting point of copper(II) chloride.[53]

The melt of the active mass of copper and potassium chlorides on carriers of different chemical nature with different specific surfaces forms isolated inclusions having a thickness equivalent to 10–200 molecular layers in the extensive pore system of the carrier.[51,54,55]

Porous substances with a wide range of specific surfaces (from 0.5–1 to 200–500 $m^2\ g^{-1}$) are used as carriers.[1,14,15] The question of the selection of the carrier is fairly specific. As a rule carriers with larger surface areas are used to effect the process in a fluidised catalyst bed rather than with a stationary bed. This is because

coarsely porous carriers having a limited surface area, used to reduce the rate of side reactions, retain the melt poorly, which leads to the sticking together of the catalyst particles when reactors with a fluidised bed are employed and appreciably impairs the process parameters.[56,57]

It has been shown[30-32,35] that hydrogen chloride is oxidised in the bulk of the salt melt. Aglulin[35] believes that the chlorination proceeds, up to 425 °C, mainly via a heterogeneous mechanism on the surface of the salt melt, while at a higher temperature the process takes place predominantly via a heterogeneous–homogeneous pathway. Another worker[58] believes that the chlorination occurs mainly homogeneously in the gas phase.

An important factor in the choice of the oxychlorination catalyst is the minimisation of side reactions involving the extensive oxidation of alkanes and the oxychlorination reaction products (chloroalkanes) to carbon oxides. The side reaction is believed to be a catalytic process[58] and it is assumed that both the carrier surface free of the salt melt[54] and the surface of the salt inclusions[59] are responsible for the occurrence of this reaction.

It appears essential to consider the individual questions concerning the use of catalysts with copper chlorides in oxychlorination processes.

At the elevated temperature (250–500 °C) normally used for oxychlorination, copper chlorides are appreciably volatile: $\lg p(\text{mm Hg}) = -3550T^{-1} + 6.55$.[60] Carriers with various physicochemical properties are used and alkali metal chlorides forming complexes with the copper salt are introduced into the system[61] in order to reduce the volatity of the active components. All these procedures make it possible to lower by 1–2 orders of magnitude the volatility of copper and to form catalysts whose operation is stable.

The use of carriers and additives stabilising copper(II) chloride makes it possible, according to Kartashov et al.,[62] to retain the activity of the catalyst during 400–500 days of continuous operation. The problem of the loss of active components is especially acute when the process is carried out in a stationary bed where local superheating of the catalyst occurs. The volatilisation of copper chlorides can alter the catalyst selectivity as a function of time as a result of the change in the Cu:K ratio in the active salt mass.

Catalysts in which the copper cations are strongly adsorbed within zeolite pores[63,64] or are chemically bound in the catalyst structure (spinels)[41] are used to reduce the volatility of copper, but such catalysts have no advantages over the usual catalysts because of the gradual change in the catalyst composition under the influence of hydrogen chloride and the high temperature.[42,65]

The question of the influence of a number of other variable-valence metals on the catalytic activity of systems based on copper compounds is of great interest. These are in the first place iron, chromium, and nickel compounds, which have been patented as activators of the above catalytic system and individual oxychlorination catalysts[1,14,15] which can also be incorporated in the catalyst as a result of the metal exchange between the reactor surface and the catalyst.[66,67] The results of studies of the influence of these additives on the activity and stability of the operation of the catalyst based on copper chlorides are contradictory, especially as regards the iron compounds. In the oxidative chlorination of dichloroethane, the introduction of chromium, nickel, and iron chlorides into the catalyst increases the conversion of the reactants and raises the yield of the target products–trichloro- and tetrachloroethylenes[68]–by a factor of 1.5–2.

In the oxidative chlorination of methane,[69] there is a sharp increase in the yield of carbon monoxide in proportion to the increase in the content of iron(III) chloride in the catalyst. The degrees of conversion of methane and oxygen do not increase while that of hydrogen chloride diminishes, because hydrogen chloride is evolved in the combustion of chloromethanes. The introduction of chromium and nickel chlorides has almost no effect on the activity of the catalyst.

The most marked increase in the rates of the Deacon and substitutional oxychlorination reactions is observed when lanthanide chlorides are added to copper and potassium chlorides.[42]

Copper(II) chloride is the dominant catalyst in the additive oxychlorination reactions[1,14,15,19,70-72] which do not include the hydrogen chloride oxidation stage. The catalytic process can be illustrated schematically in relation to the oxychlorination of ethylene (Scheme 3):

Scheme 3

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + Cu_2Cl_2 ,$$
$$Cu_2Cl_2 + 2HCl + 0.5O_2 \rightarrow 2CuCl_2 + H_2O .$$

The formation of univalent copper has been confirmed by X-ray diffraction data for the catalyst.[73]

In view of the wide-scale industrial use of the oxidative chlorination of ethylene, the choice of the appropriate catalysts is of great practical interest. Almost all the catalysts include, apart from copper(II) chloride, various additives, which depend on the process temperature. Allen and Clark[16] showed that the activity of the catalyst for the oxychlorination of ethylene increases appreciably when yttrium chloride is added. The useful life of the catalyst also increases under these conditions. Alumina is used preferentially as the carrier, but activated charcoal, silica gel, aluminosilicate, zeolites, and other carriers can also be used.[1,14,15]

The oxychlorination of ethylene in the presence of the catalyst with copper(II) chloride deposited on different carriers, including alumina or activated charcoal, takes place at 210–280 °C and the yield of 1,2-dichloroethane is at the level of 99%.[15,17] An increase in temperature promotes the acceleration of the substitutional oxychlorination and dehydrochlorination, which results in the formation of considerable amounts of vinyl chloride, polychloroethanes, and di-, tri-, and tetra-chloroethylenes.[1,74]

The choice of the carrier is very important for the activity of the catalyst. On the basis of the analysis of literature data, it has been concluded[1,14,15,20] that the greatest activity in the temperature range 200–260 °C is shown by catalysts based on alumina. An increase in temperature lowers the selectivity in the formation of dichloroethane and even leads to the loss of activity by the catalyst. It has been shown[75-78] that the activity and selectivity of the action of the catalyst depend to a great extent on the phase composition of the alumina. The use of η- or κ-Al_2O_3 [77] leads to an almost 100% yield of dichloroethane at 200–240 °C. According to Flid et al.,[75] when the process is carried out in a "fluidised" catalyst bed, it is useful to employ microspherical alumina containing the α-, θ-, and γ-forms in the proportions 1:2:4.

The content of the θ-phase of Al_2O_3 in the carrier plays a major role. The deposited copper(II) chloride reacts with it to form copper aluminates with spinel structures. The copper then exists on the surface both as $CuCl_2$ and as hydroxide chlorides, whose structure depends on the carrier. It is claimed[78] that the increase in the activity of the catalyst is associated with the increase in porosity, the content of the θ-phase, and the number of basic centres on the carrier surface.

The question of the effect of catalyst poisons on the ethylene oxychlorination catalyst is of great practical importance.[79] This problem has so far been inadequately investigated, but there are data showing that the activity of the catalyst decreases when sulphur compounds enter this system.[80,81]

It is claimed[80] that the deactivation is associated with the formation of the inactive copper sulphate and hence with the decrease in the content of copper(II) chloride in the catalysts, which leads directly to a decrease in activity.

The authors of the present review hold another view. It has been established[81] from IR spectroscopic data that copper sulphate is not formed under the reaction conditions. The impairment of the process parameters is associated, in our view, with the reduction of Cu^{2+} to Cu^{+} by sulphur dioxide and the reduction of copper(II) chloride by ethylene, which competes with the above reaction, and also with the blocking by the sulphur-containing ions of the centres on the carrier surface participating in the reaction. It has been suggested that the surface sulphur-containing structures be removed in order to restore the activity of the catalysts.[81]

It is of great interest to carry out the oxychlorination of ethylene at elevated temperatures (350–500 °C). Under these conditions, the process is performed in the presence of catalysts with the traditional mixture of the catalytically active components. The main difference consists in the employment of carriers more resistant to the action of high temperatures than alumina. They include primarily silica gel, α-alumina, and celite.[82] The possibility of using catalysts containing lanthanide metal chlorides together with copper and alkali metal chlorides has been considered.[82] The selectivity in the formation of vinyl chloride in the oxychlorination of ethylene at such temperatures reaches 92%.[83] The employment of the $CuCl_2-KCl$ catalyst on silica gel and of the $FeCl_3-KCl-La_2O_3$ catalyst on celite at 500 °C makes it possible to achieve a yield of vinyl chloride up to 50%.[15] At lower temperatures (370–430 °C) and when the $CuCl_2-KCl-PrCl_3$ catalyst on microspherical silica gel is used, the main products are tri- and tetra-chloroethylene (selectivity up to 80%).[84]

Vinyl chloride can be obtained also at temperatures in the range 200–300 °C by using primarily catalysts containing platinum group metal compounds together with copper and iron.[15,20,85-87] The presence of copper and iron compounds in the catalyst is evidently essential for the oxidation of the platinum group metals (Scheme 4):[87]

Scheme 4

$$C_2H_4 + PdCl_2 \rightarrow C_2H_3Cl + Pd + HCl\ ,$$
$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl\ .$$

The method of preparation of the catalyst has a great influence on its properties, including the selectivity and stability of its operation.[87] It has been established in the synthesis of the $Pd-Fe/Al_2O_3$ catalytic system that the optimum stability of operation of the catalyst is observed when the α- and θ-forms are present in the Al_2O_3,[87] which agrees with the data on the low-temperature oxychlorination described above.

The catalyst activity series for the formation of vinyl chloride is Pd > Rh > Pt > Ru; the highest selectivity has been achieved using palladium. A disadvantage of the catalysts described is the limited conversion of ethylene.

The main pathway in the oxychlorination of chloroethanes and chloroethylenes involves the formation of tri- and tetra-chloroethylenes.[1,15,20] The oxychlorination of chloroethylenes can be carried out in the presence of the catalyst described above at 200–300 °C and involves the addition of chlorine to the double bond.[1,88] An increase in the oxychlorination temperature to 400 °C makes it possible to obtain also tri- and tetra-chloroethylenes with fair selectivity (to an extent greater than 80%).[84,88] Tetrachloroethylene also can be obtained[89] by oxidising tetrachloroethane or other chloroethanes with a high chlorine content at 390 °C in the presence of the traditional oxychlorination catalyst.

Under the conditions of the high-temperature oxychlorination of chlorohydrocarbons of the ethane–ethylene series, the carrier has a much smaller influence on the properties of the catalyst. This applies especially to the process in a stationary catalyst bed. It has been shown[90] that the use of carriers greatly differing in chemical composition (Al_2O_3, SiO_2, $Al_2O_3-SiO_2$) and also in the specific surface and porosity in the oxychlorination of 1,2-dichloroethane leads to similar results as regards the conversion of the reactants and the selectivity in the formation of the target products.

Two main pathways must be distinguished in the oxychlorination of C_3 hydrocarbons: the synthesis of allyl chloride from propene and of organochlorine solvents (tri- and tetra-chloroethylenes, carbon tetrachloride) from different types of raw material.

In in the oxychlorination of propene in the temperature range 150–350 °C in the presence of the copper-based catalyst, the main product is 1,2-dichloropropane.[1,14,15,91] An increase in temperature leads to the appearance of appreciable amounts of allyl chloride in the products, but it also greatly accelerates the extensive oxidation side reactions and the loss of copper.

The principal procedure for increasing the selectivity in the formation of allyl chloride at relatively low temperatures (150–300 °C) involves the use of catalysts containing compounds of platinum group metals and tellurium. The possibility of the selective formation of allyl chloride at 180–240 °C in the presence of a catalyst containing platinum group metals on a carrier has been indicated.[90] The catalytic activity of the metals varies as follows: Rh > Pd > Pt > Ir > Ru; activated charcoal is the best carrier. It has been shown that the use of a mixture of platinum group metal, copper, and lanthanide chlorides[15,87,92] greatly increases the rate of reaction. The selectivity in the formation of allyl chloride reaches 90%. The mechanism of the action of the catalyst is analogous to that described for ethylene (see Scheme 4). The presence of platinum group metals in the catalyst virtually rules out the formation of 1,2-dichloropropane and the main side product is isopropyl chloride. The stability of the operation of this catalytic system is ensured by alkali metal chlorides, the best of which is sodium chloride[87,92] which does not impair the selectivity of action of the catalyst.

The use of tellurium compounds ensures a selectivity in the formation of allyl chloride at the level of 90% and above.[93] The presence of alkali metal chlorides lowers the selectivity and it is desirable that the catalyst should contain platinum group metal compounds in order to increase it.[94]

The oxychlorination of C_3 hydrocarbons and their chloro-derivatives is frequently carried out in order to obtain organochlorine solvents, traditional and modified catalytic systems being used for this purpose at temperatures which are as a rule above 350 °C. The reaction product consists of a complex mixture of hydrocarbons, the target products being tri- and tetra-chloroethylenes and carbon tetrachloride.[13,63,95]

IV. THE KINETICS AND MECHANISMS OF THE OXYCHLORINATION REACTIONS

It has been established in the course of a whole series of investigations[18,31,35,36] that the high-temperature oxychlorination proceeds via a stage involving the oxidation of hydrogen chloride to chlorine. The mechanism of the oxidation of HCl was described in the Section dealing with the catalysts and the kinetics of this reaction have been fairly well investigated.[18,29,30,etc] One can only state that the probabilities of the possible type of mechanisms of this reaction have been estimated[18] in accordance with the available experimental data.

Despite the definite differences between the postulated mechanisms of the Deacon reaction and even the disagreement concerning the region where it occurs (on the surface or in the bulk of the melt),[27,29,35] the rate of reaction r is described in all cases by equations of the following type after some simplification:

$$r = \frac{k\, p_{O_2}}{p_{Cl_2}}\ .$$

Until recently, the kinetics and mechanism of the oxychlorination of methane had been little investigated. It was established[96] that the chlorination of methane in the melts occurs at higher rates than the thermal process, the authors suggested that this takes place as a result of the iniation of the gas-phase process by the chlorine atoms evolved from the surface of the melt. This view was questioned[97] on the grounds that the rate of evolution of chlorine in the thermal decomposition is much lower than the rate of chlorination and also because of the difference between the selectivities in the gas-phase and catalytic chlorinations. This suggests that the chlorination of methane takes place predominantly directly in the melt.[97]

Other workers,[18,31,32,35] who have studied the kinetics and mechanism of the methane oxychlorination reaction in greatest detail, hold an analogous view. It has been shown that the oxidation of HCl takes place throughout the bulk of the melt with participation of $CuCl_2$ (see Scheme 2) regardless of the subsequent chlorination of methane, which is indicated by the same kinetics being observed when the reaction is studied in the presence and absence of methane.

It is believed[31,32,35] that the chlorination of methane up to 425 °C takes place on the surface of the melt predominantly via the interaction of methane with a polyhalide complex of the type ZCl_3, formed when molecular chlorine is chemisorbed by metal chlorides, Z being the free catalytic centre:

$$ZCl + Cl_2 \rightleftarrows ZCl_3 (ZCl \cdot Cl_2) ,$$

$$ZCl_3 + RH \rightleftarrows RCl + HCl + ZCl .$$

An increase in temperature increases the contribution of the reaction involving the thermal bulk-phase chlorination by free chlorine. It has been concluded[35] that the melt-free catalyst surface is virtually uninvolved in the chlorination reaction. The hypothesis has been put forward that metal chlorides inhibit the reaction in the bulk phase because of their greater affinity for chlorine.

Since the rate and kinetics of the chlorination of methane depend little in practice on the changes in the composition of the $CuCl_2-KCl$ system, the introduction of $LaCl_3$, or the replacement of $CuCl_2$ by LiCl, the authors suggest that the participation of variable-valence metal chlorides in complexes of the type ZCl_3 ($ZCl.Cl_2$) is not obligatory and that chlorination can take place on catalytic centres different from those which are essential for the oxidation of HCl.

The reactions involving the oxidative and direct chlorination of methane in the presence of salt catalysts are described by the same kinetic equation,[31,32,35] i.e.

$$r = k p_{CH_4} p_{Cl_2}^{0.6} p_{O_2}^{n} ,$$

in which the order with respect to oxygen (n) varies with temperature from 0 to -0.25. Depending on the nature of the salt, the observed activation energy varies from 84 to 113 kJ mol^{-1}.

The use of semiconductor detector, mass-spectrometric, and molecular beam methods enabled Gel'bshtein and Bakshi[98] to justify the hypothesis of the heterogeneous-homogeneous character of the chlorination stage in the substitutional oxychlorination of alkanes.

The main side products in the oxychlorination of methane are carbon oxides. The rate of oxidation of methane and its chloro-derivatives is characterised by being first order with respect to the organic substrate and oxygen, while the ratios of the rates are $r(CH_3Cl) : r(CH_2Cl_2) : r(CHCl_3) : r(CH_4) : r(CCl_4) = 1 : 0.5 : 0.33 : 0.18 : 0.033$. The selectivity in the formation of CO increases with increase in the partial pressure of HCl.[32,35] The mechanism of the extensive oxidation reactions has been scarcely investigated.

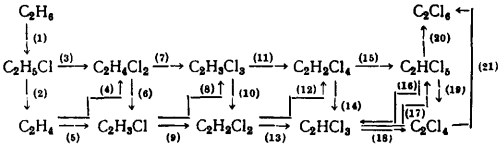
The occurrence of the partial oxidation reactions of chloroethanes and chloromethanes as well as the formation of condensation products (carbon black formation) has been indicated in most studies. It has been established[99] that, at elevated temperatures in the absence of oxygen, carbon is deposited on the catalyst in the decomposition of chloromethanes. In the normal course of the process, the decomposition of condensation products were burnt off by oxygen with formation of oxides, which agrees with Mamedov's data.[63]

The kinetics of the oxychlorination of methane in the presence of the spinel copper–chromium catalyst have been described[100] and an equation has been obtained for the overall rate: $r = k p_{CH_4}^{0.8} p_{O_2}^{0.4}$, with an activation energy of 155 kJ mol^{-1}.

The kinetics and mechanism of the high-temperature oxychlorination of ethane, propane, and their chloro-derivatives have been studied in less detail because of its much greater complexity compared with the oxychlorination of methane. Only the formation of chlorine and its involvement in the reactions of the hydrocarbons are unquestionable.[1,15,36,37,98] According to the results of Gel'bshtein and Bakshi,[98] the chlorine formation and chlorination reactions take place on different active centres.

When account is taken of the subsequent reactions of the intermediates, the oxidative chlorination of ethane consists of a heterogeneous-homogeneous process, which proceeds via a series of parallel-consecutive chlorination and dehydrochlorination stages and is accompanied by the oxidation of the starting materials and intermediates to carbon oxides. The simplified mechanism of the formation of the reaction products can be represented as follows (Scheme 5):[36,37,101]

Scheme 5



Depending on the conditions, the process can be directed towards the formation of chloroethylene (vinyl chloride) or towards more chlorinated products.

In view of the large number of individual reactions, the oxychlorination of ethane has been studied in stages. The observed rates of reaction of ethylene, ethane, chloroethane, 1,2-dichloroethane, chloroethylene[36,37] and also the rates r_{16}, r_{18}, and r_{19} [106] are described satisfactorily by the equation

$$r_i = k_i p_i p_{Cl_2}^{0.5} . \qquad (I)$$

The rates of reaction of 1,1-dichloroethane depend solely on its partial pressure.

The following reaction pathways in Scheme 5 have been discovered:[18,56,57,102] (a) chloroethane is converted into 1,1-dichloroethane, 1,2-dichloroethane, and ethylene; (b) 1,2-dichloroethane is converted into 80% chloroethylene and 20% 1,1,2-trichloroethane; (c) ethylene, chloroethylene, and dichloroethylene are chlorinated only additively; (d) chloroethylene is formed as a result of the dehydrochlorination of both dichloroethanes; (e) 1,1,2-trichloroethane is formed from chloroethylene and 1,2-dichloroethane but not from 1,1-dichloroethane.

It has been shown[103] that the oxychlorination of ethylene and chloroethylene take place with participation of the catalyst. Ethane, chloroethane, and 1,2-dichloroethane react with molecular chlorine via a radical-chain mechanism, while the dehydrochlorination of 1,1-dichloroethane and the dissociation of chlorine into atoms take place with participation of the catalyst.[104]

According to some data,[105,106] 1,1,2-trichloroethane is formed via both 1,2-dichloroethane and via chloroethylene, while the relative contributions of these pathways depend in the first place on the volume of the gas phase in the reactor.[106]

The observed rate constant in Eqn. (I) depends on the nature of the organic substrate and decreases in the sequence $C_2H_6 > C_2H_5.Cl > C_2H_4Cl_2$ for saturated compounds. The activation energies for the conversion of the saturated (130 kJ mol^{-1}) and unsaturated

compounds (40–90 kJ mol^{-1}) differ very markedly, as a result of which the yield of alkenes increases with increase in temperature.

In the oxychlorination of hydrocarbons of the ethane–ethylene series, extensive formation of carbon oxides takes place. The rates of these reactions described [36,37] by the empirical equation

$$r_{CO+CO_2} = k_i p_i p_{O_2} p_{Cl_2}^{0.5} \quad .$$

The main contribution to the formation of carbon oxides comes from unsaturated compounds.[6,37,87,89] The introduction of one chlorine atom into ethylene increases the observed extensive oxidation rate constant by a factor of 7–8, while further increase in the chlorine content in the molecule diminishes the degree of combustion of chloroalkenes.[36,37]

The kinetics and mechanism of the high-temperature oxychlorination of C_3 chloroalkanes, which proceeds with formation of tri- and tetra-chloroethylenes and carbon tetrachloride, have been investigated.[13,63,95] In the oxychlorination of 1,2-dichloropropane by the $Cl_2 + O_2$ mixture in the temperature range 310–390 °C in the presence of the $CuCl_2$–KCl catalyst on a carrier, it has been established[13] that the rates of decrease in the amounts of all the reactants are described by the general equation

$$r = k_i p_{C_3H_6Cl_2}^{0.7} p_{Cl_2}^{0.3} (1 + p_{O_2}) \quad .$$

It has been suggested that the reaction take place both in the bulk phase and on the catalyst, which agrees with the results of studies on the high-temperature oxychlorination of ethane, ethylene, and their chloro-derivatives presented above.

The additive oxychlorination of alkenes takes place on catalysts with $CuCl_2$ at much lower temperatures (200–300 °C) than the oxychlorination of alkanes and does not involve the HCl oxidation stage (see Scheme 3). The kinetics of the oxychlorination of ethylene and propene have been studied on a series of catalysts under different conditions and have been described in detail in several reviews.[1,14,15,20,107] The empirical equations proposed for the reaction rates differ appreciably depending on the catalyst and the process conditions.

The first kinetic study of the oxychlorination of ethylene was carried out[108] on the $CuCl_2$–Al_2O_3 catalyst at 200–300 °C. The authors claimed that the rate of the process is independent of $p_{C_2H_4}$ but does depend on p_{O_2} and also that the reaction is inhibited by dichloroethane and HCl. In subsequent investigations, these conclusions were not in the main confirmed. It was found[107,109] that the rate of reaction depends in a complex manner on the partial pressures of ethylene, HCl, and oxygen and is described by a power equation of the type

$$r = k\, p_{C_2H_4}^{m} p_{HCl}^{n} p_{O_2}^{l} \quad . \qquad (II)$$

In the presence of the $CuCl_2$–KCl/silica gel catalyst in the region of limited conversions of ethylene, the parameters in Eqn. (III) are $m = 0.6$, $n = 0.2$, and $l = 0.5$. In the presence of a catalyst based on Al_2O_3 a direct dependence of the rate $p_{C_2H_4}$ and p_{O_2} ($m, l = 1$) and a weak dependence on p_{HCl} ($n = 0.3$) in the region of low oxygen pressures have been established; when $p_{O_2} \geqslant 0.01$ MPa, we have $l = 0$. An analogous picture ($m = 1$, $n = 0.2$, and $l = 0$) is observed when the $CuCl_2$/activated charcoal catalyst is used in the temperature range 130–180 °C; the selective formation of dichloroethane is possible only under the conditions of an excess of ethylene.

On the other hand, it has been stated[109] that, when an Al_2O_3-based catalyst is used, the rate of reaction depends on $p_{C_2H_4}$ and p_{O_2} but is independent of p_{HCl}, which is evidence, according to the authors, that the rate of reaction is limited by the stage involving the interaction of ethylene with oxygen on the catalyst surface.

The most complete idea about the kinetics and mechanism of the additive oxychlorination of alkynes has been put forward in studies by Gel'bshtein and co-workers.[110-112] The addition to the catalyst of alkali metal chlorides, capable of being coordinated to the copper cation as well as the adsorption of hydrogen chloride increase the electron density on the copper cation and thereby increase the dative component in the interaction of the copper cation with the olefin and at the same time weaken the Cu–Cl bond. The dissociation of two such bonds results in the addition of chlorine atoms to the olefin and in the corresponding reduction of the copper cation in the active centre.

The following mechanism of the reactions (Scheme 6) has been proposed for the oxychlorination of ethylene (at 250–340 °C in the presence of the $CuCl_2$–KCl catalyst on aluminosilicate or silica gel):[110,111]

Scheme 6

		(A)	(B)
$[Cu_mCl_n] + HCl \rightleftarrows [Cu_mCl_n \cdot HCl]$	(1′)	1	1
$[Cu_mCl_n \cdot HCl] + HCl \rightleftarrows [Cu_mCl_n \cdot 2HCl]$	(1″)	1	0
$[Cu_mCl_n \cdot 2HCl] + C_2H_4 \rightarrow [Cu_m^{2-}Cl_{n-2} \cdot 2HCl] + C_2H_4Cl_2$	(2)	1	0
$[Cu_m^{2-}Cl_{n-2} \cdot 2HCl] + O_2 \rightarrow [Cu_mCl_{n-2} \cdot 2HCl \cdot O_2^{2-}]$	(3)	1	0
$[Cu_mCl_{n-2} \cdot 2HCl \cdot O_2^{2-}] + C_2H_4 + 2HCl \xrightarrow{fast} [Cu_mCl_n] + C_2H_4Cl_2 + 2H_2O$	(4)	1	0
$[Cu_mCl_n \cdot HCl] + C_2H_4 \rightleftarrows [Cu_mCl_n \cdot HCl \cdot C_2H_4]$	(5)	0	1
$[Cu_mCl_n \cdot HCl \cdot C_2H_4] + O_2 \xrightarrow{+2O_2} [Cu_mCl_n] + 2CO_2 + 2H_2O$	(6)	0	1

$2C_2H_4 + 4HCl + O_2 \rightarrow 2C_2H_4Cl_2 + 2H_2O$ (A)

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ (B) .

The numerals designating the stages and the stoichiometric numbers of these stages via pathways (A) and (B) are indicated to the right of the chemical equations.

If it is assumed that stages (1′), (1″), and (5) of Scheme 6 correspond to equilibrium, then the kinetic equations corresponding to the proposed Scheme and describing the rates of formation of 1,2-dichloroethane (r_A) and carbon dioxide (r_B) are as follows:

$$r_A = 2\,\frac{K_1' K_1'' k_2 p_{HCl}^2 p_{C_2H_4}}{1 + K_1' p_{HCl}\left[1 + K_5 p_{C_2H_4} + K_1'' p_{HCl}\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)\right]}, \qquad (III)$$

$$r_B = \frac{K_1' K_5 k_6 p_{HCl} p_{C_2H_4} p_{O_2}}{1 + K_1' p_{HCl}\left[1 + k_5 p_{C_2H_4} + K_1'' p_{HCl}\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)\right]} . \qquad (IV)$$

On the assumption that

$$K_1'' p_{HCl} \gg 1 + K_5 p_{C_2H_4}$$

Eqn.(III) assumes the form

$$r_A = 2\,\frac{K_1 k_2 p_{HCl}^2 p_{C_2H_4}}{1 + K_1 p_{HCl}^2\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)} ,$$

where

$$K_1 = K_1' K_1''$$

On the same assumption, Eqn. (IV) can be written in the form

$$r_B = \frac{K_1' K_5 k_6 p_{HCl} p_{C_2H_4} p_{O_2}}{1 + K_1 p_{HCl}^2\left(1 + \frac{k_2 p_{C_2H_4}}{k_3 p_{O_2}}\right)} .$$

Under conditions where $p_{O_2} \geqslant (p_{O_2})_{min}$ and $p_{HCl} \geqslant (p_{HCl})_{min}$, the rate of reaction is described by a simple first-order equation with respect to ethylene: $r = k_{obs} p_{C_2H_4}$.

The oxychlorination reaction of ethylene in the $CuCl_2$–KCl/γ-Al_2O_3 catalytic system has been investigated in detail.[113] The authors established that the maximum rate of formation of dichloroethane in the temperature range 220–300 °C corresponds to

a copper concentration in the catalyst of ~7.5%. The rate of formation of side products, in particular of ethyl chloride, CO, and CO_2, falls sharply with increase in the copper concentration. Kinetic studies confirmed the inhibition of the CO and CO_2 formation reactions by hydrogen chloride. It has also been shown that an increase in the Cu/K ratio lowers the activation energy for the dichloroethane formation reaction.

The kinetics of the oxychlorination of ethylene on the $PdCl_2-FeCl_3/\gamma\text{-}Al_2O_3$ catalyst at 230–280 °C have been studied.[87] The main products are chloroethylene and chloroethane whose rates of formation are described by Eqns. (V) and (VI):

$$r_{C_2H_3Cl} = k\, p_{C_2H_4}^{0.9}\, p_{O_2}^{0.6}\ , \qquad (V)$$

$$r_{C_2H_5Cl} = k'\, p_{C_2H_4}^{0.5}\, p_{HCl}^{0.8}\, p_{O_2}^{0.6}\ . \qquad (VI)$$

Analysis of Eqns. (V) and (VI) shows that chloroethylene and chloroethane are formed on different catalytic centres, since the orders with respect to HCl and C_2H_4 are different for these reactions.

The presence of zerovalent palladium and Fe^{2+} in the catalyst leads to an appreciable increase (by a factor of 2–3) in the degree of chemisorption of O_2. Evidently the catalyst surface is occupied by the palladium–iron complex with chemisorbed oxygen on which the main reaction products are in fact formed, which explains the identical reaction orders with respect to oxygen in Eqns. (V) and (VI).

The picture is similar in the oxychlorination of propene. The rate of reaction depends on the concentration of Pd and $PdCl_2$ in the catalyst and also on $p_{C_3H_6}$.[114] The kinetics of the oxychlorination of propene to 1,2-dichloropropane on the $CuCl_2-KCl/Al_2O_3$ catalyst have been studied.[112] The principal features are analogous to those obtained for ethylene. The rate of reaction at $p_{HCl} \geqslant 2$ kPa is described by the equation

$$r = k' p_{C_3H_6} \Big/ \left(1 + \frac{k' p_{C_3H_6}}{k'' p_{O_2}}\right)\ .$$

Depending on the conditions, the rate of the reaction is first order with respect to propene with an activation energy in the range of 90 kJ mol^{-1} or first order with respect to oxygen with an activation energy at the level of 30 kJ mol^{-1} (for zero reaction orders with respect to the other reactants).

V. THE TECHNOLOGY OF THE PROCESSES

This Section deals mainly with questions concerning the oxychlorination reactor – the most complex unit in the process.

In industrial practice the oxychlorination is carried out in different reactors,[1,14,15,20] for example on fluidised,[115,116] and stationary catalyst beds,[117] and also in melts.[73] A highly isothermal process can be achieved in a fluidised bed, but, when the latter is employed, considerable complications arise in connection with the recovery of the catalyst, the corrosion of the heat exchange elements, the low conversion of the reactants, and the poor susceptibility to modelling. In reactors with a stationary bed considerable local superheating can occur, which leads to vigorous side reactions involving extensive oxidation. They are distinguished by an appreciably lower productivity but make it possible to achieve a high conversion of the reactants.[117,118]

The use of a combination of reactors with a fluidised bed (the first in the set-up for the process) and a stationary bed makes it possible[119] to create a set-up with a high productivity and a high conversion of the reactants.

Comparative study of the oxychlorination of methane in reactors with fluidised and stationary catalysts and also in the melt showed[120] that satisfactory results can be achieved under certain conditions.

When reactors with a fluidised catalyst bed are used, much attention is devoted to the conditions governing the fluidisation and mixing of the reactants. In order to eliminate the influence of backmixing and breakthrough in the form of bubbles, it was recommended that the reactor diameter be restricted to 100–500 mm,[121] which ensures minimal combustion as a result of uniform fluidisation without gas bubbles. In order to create set-ups with a high unit productivity, several tubes of this diameter are combined in a single jacketed tubular reactor. The removal of heat in the reactors is achieved with the aid of heat exchange elements[122] or by recycling the products.[123] To prevent the possibility of the decay of the reaction, it is recommended that the temperature of at least some of the heat exchange elements should differ from the temperature of the bed by not more than 25 °C.[122] Satisfactory mixing of the reactants promotes an increase in selectivity and is carried out directly in the fluidised bed,[115] in pre-mixers with a fluidised bed of inert materials,[124] or in special devices with a wide variety of designs.[125]

The oxychlorination stage is used mainly to establish processes, balanced with respect to chlorine, in which organochlorine products are obtained. The high-temperature chlorination is usually carried out in the first stage, while the hydrogen chloride from the chlorination stage is supplied to the oxychlorination stage, the products being either isolated from the reaction gas[126] or also supplied to the oxychlorination stage.[127] The supply to the oxychlorination stage of the same hydrocarbon raw material as in the chlorination stage is economically most efficient, since in this case there are no problems with the purification of hydrogen chloride.

Oxychlorination with a mixture of chlorine and oxygen or air is also known.[1,13,14,20,21,63,128,129] In this case the chlorination and oxychlorination reactions are combined in a single reactor; when polychlorides with a high chlorine content are processed under the conditions of a low heat change, this procedure is especially advantageous. Oxychlorination using chlorine takes place more vigorously, but, when C_2 and C_3 polychlorides are used, the contribution by extensive oxidation side reactions increases, in the first place owing to dehydrochlorination and the formation of alkenes which exhibit an increased tendency towards the formation of carbon oxides.[92,116] The yield of oxides is reduced by the means of an oxygen supply divided into sections along the height of the reactor[13,95,116,128,129] as a result of which the oxygen comes into contact not with the initial raw material but with more chlorinated hydrocarbons. The oxychlorination with a $Cl_2 + O_2$ mixture is carried out in reactors of all types, although it is assumed that the preferred variant involves the process being carried out in a pseudofluidised catalyst bed or in the melt.[13,128,129]

Processes in which hydrogen chloride is used have become the most common. There is also a possibility of employing hydrochloric acid.[130,131] The presence of large amounts of water vapour in the reaction mixture makes it possible to carry out the process successfully in a stationary bed – there is virtually no superheating of the catalyst in this case.[131] However, an excess of water vapour can also lead to the occurrence of side reactions. Thus reactions involving the formation of allyl alcohol, acrolein, and other oxygen-containing products are appreciably accelerated in the case of propene.[132] The interaction of chloroethylene with water vapour to form ethylene has been observed at temperatures above 450 °C.[133]

Air, air enriched in oxygen, and concentrated oxygen can be used as oxidants for oxychlorination.[128,129,134,135] The replacement of air by oxygen can greatly increase the productivity of the reactors, can simplify the condensation scheme by increasing the concentrations, and ultimately can reduce the intrinsic cost of the products. Under conditions where oxygen is used, the requirements for the removal of heat and conditions free from the risk of explosion become much more stringent, so that it is recommended that a reactor with a

fluidised catalyst bed be used for this purpose.[21,22,134,135] However, the possibility of the successful employment of concentrated oxygen also in reactors with a stationary bed has been demonstrated.[128,129] Provided that the conditions are chosen correctly, the selectivity in the formation of the target products is at the same level as in the case where air is used.

Oxidative chlorination has been used much less than the chlorination method because of the following disadvantages: (1) the volatility of the active components of the catalyst; (2) the formation of extensive oxidation side products ($CO + CO_2$) and the insufficiently high conversions of the reactants and yields of the target products (especially in the high-temperature process); (3) the pronounced corroding effect of the medium (catalyst, hydrogen chloride, chlorine, and water vapour at a high temperature).

The loss of copper(II) chloride from the catalyst is compensated by passing the initial reaction mixture through a melt or solid carrier containing copper(II) chloride.[136] When the oxychlorination is carried out in a fluidised bed, a constant amount of the catalyst is maintained by adding the solid carrier, copper in the form of the metal or a salt, and also an alkali metal as the chloride.[137]

In order to reduce the yield of carbon oxides and to improve the selectivity in the formation of target products, attempts are made in the first place to achieve the optimum temperature conditions in the oxychlorination reactions. It is recommended that the process be carried out in the presence of a (5–20)-fold excess of hydrogen chloride to maintain a uniform temperature in the catalyst bed.[138]

The attempts to organise temperature fields in reactors with a stationary catalyst bed by arranging the catalyst in order of increasing activity along the gas stream,[139] by a stepwise increase in the size of the catalyst particles,[140] and by increasing the tube diameter or by means of a higher temperature in each successive (along the gas stream) catalyst bed[141] are noteworthy.

The uniform mixing of active and low-activity catalysts increases[142] the yield of the target product by increasing the selectivity of the main reaction. The procedures described activate the process in the terminal part of the reactor and make it possible to achieve a high conversion of HCl.

It is also recommended that the catalyst be diluted by an inert material with a high thermal conductivity: graphite,[143] silicon carbide,[144] metals (nickel, molybdenum, cobalt, and silver) and their alloys,[145] and also the unimpregnated carrier.[146]

Only chloromethanes are recycled in the chlorination stage and only methane, oxygen, nitrogen, and carbon oxides are recycled in the oxychlorination stage in order to increase the degree of the useful employment of chlorine and to reduce the formation of side products.[147]

The greatest effect in reducing the extensive oxidation side reaction can be achieved by preventing contact between the hydrocarbon and oxygen by carrying out the process in two stages. In the first stage, the hydrocarbon is chlorinated with the aid of, for example, copper chloride, while in the second stage the reduced form of copper is oxidised by oxygen and hydrogen chloride. A melt of copper and potassium salts is usually employed to achieve such a process.[23,24,120,148] The low conversion of the hydrocarbons and the complexity of the equipment for transporting the melt should be included among the disadvantages of this method. In order to simplify the transfer of the catalyst from one stage to the other, it is suggested[149] that the traditional catalyst with $CuCl_2$ on a carrier be used. However, the formation of carbon oxides cannot be fully avoided even when a two-step scheme is used, since the oxidised form of the catalyst, coming into contact with the hydrocarbon, contains copper oxide chloride, which leads to the formation of carbon oxides.

Attempts have been made to reduce the corroding effect of the catalyst on the reactor material by selecting appropriately the carrier and the composition of the active mass,[150] but these improvements are not of fundamental importance. It has therefore been suggested that, when the process is carried out in a stationary bed, the surface of the tube should be coated with glass[140,151] or that a lined adiabatic reactor be employed.[152]

A procedure in which the oxychlorination process is initiated by means of a correct sequence in the supply of the reactants to the catalyst heated beforehand has been patented.[153] A method for the elimination of iron(III) chloride from the initial reactants[154] in order to maintain the activity and selectivity of the oxychlorination catalyst based on copper chlorides has also been proposed.

The above improvement in the technological set-up for the process permits the expectation of an expansion in the employment of the oxychlorination method at the present.

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