STUDY OF METHANE OXYCHLORINATION REACTION

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Abstract. The article investigated the methane oxychlorination reaction in a flow reactor and selected a catalyst containing \( (\text{CuCl}_2)_x : (\text{KCl})_y : (\text{ZnCl}_2)_z : (\text{MnCl}_2)_k / \text{HSZ} \) (high-silicon zeolite) with high activity, selectivity and efficiency. The influence of various factors on the rate of the methane oxychlorination reaction and the yield of the reaction products in the presence of the selected catalyst was studied. Based on the results obtained, the kinetic laws of the reaction were investigated and the following optimal conditions for the methane oxychlorination reaction were selected: \( (\text{CuCl}_2)_x : (\text{KCl})_y : (\text{ZnCl}_2)_z : (\text{MnCl}_2)_k / \text{HSZ} \)-containing catalyst, \( T = 340 \) °C, \( \tau = 0.1 \) second, \( N_2 : CH_4 : HCl : O_2 = 5 : 14 : 2 : 1 \) volume ratio, \( P = 0.1 \) MPa, size of catalyst fractions \( 0.7 \div 1.2 \) mm, gas flow rate \( 17 \), \( 2 \) l/h, contact time \( 0.1 \), linear flow rate \( 10.2 \) cm / sec.

Introduction. Ethylene is the most widely used organic product worldwide and is widely used as a primary semi-product in the chemical and petrochemical industries. Currently, the annual demand for ethylene is more than 180 million tons. Currently, the main feedstock for the production of ethylene and propylene is naphtha (gasoline fraction of direct oil transfer) and compressed hydrocarbons [1-5].

Today, the following methods for producing ethylene are of great interest to scientists in world practice:
1) Oxidative dimerization of methane;
2) by recovering methane chloride from methane and its pyrolysis;
3) Synthesis gas from methane and methanol and ethylene recovery from methanol.

Among the methods mentioned above, the catalytic oxidation and dimerization (oxycondensation) reaction of methane is a step-by-step method at normal atmospheric pressure, a method that has not yet been introduced into the industry. However, laws, mechanism, kinetics and other reaction parameters have been studied in detail. To date, catalysts with high catalytic activity, selectivity and efficiency have been developed for this reaction. Such catalysts include those containing \( \text{MeMnW} / \text{SiO}_2 \) \( (\text{Me} = \text{Li}, \text{Na}, \text{K}) [6-9] \) and \( \text{(MoO}_3)_x (\text{ZnO})_y (\text{ZrO}_2)_z \) [10-18].
The second method, the process of producing ethylene from natural gas through methanol, involves the following reactions:

1. Synthesis gas production:

   \[
   \begin{align*}
   CH_4 + H_2O & \rightleftharpoons CO + 3H_2 & -206 \text{ kJ/mol} \\
   CH_4 + CO_2 & \rightleftharpoons 2CO + 2H_2 & -247 \text{ kJ/mol} \\
   CH_4 + 1/2O_2 & \rightarrow CO + 2H_2 & +36 \text{ kJ/mol}
   \end{align*}
   \]

2. Extraction of methanol:

   \[
   CO + CO_2 + 5H_2 \rightarrow 2CH_3OH + H_2O \\
   T=220-280^0C; \ P = 5-10 \text{ MPa}, Cu/Zn catalyst [19].
   \]

3. Conversion of methanol in the presence of a catalyst:

   \[
   nCH_3OH \rightarrow C_2H_4 + C_3H_6 + C_4H_8 + C_nH_{2n} + nH_2O
   \]

The third method involves the reaction of obtaining ethylene by pyrolysis of methyl chloride obtained by oxidizing methane. The main reactions that take place in this process are as follows:

\[
\begin{align*}
2CH_4 + 2HCl + O_2 & \leftrightarrow 2CH_3Cl + 2H_2O \Delta H=157 \text{ kJ/mol} \\
nCH_3Cl & \rightarrow C_2H_4 + C_nH_{2n} + nHCl \Delta H=-10-70 \text{ kJ/mol}
\end{align*}
\]

However, there is also a coking reaction:

\[
CH_3Cl \rightarrow C + H_2 + HCl \Delta H=-10,3 \text{ kJ/mol}
\]

The main catalysts for methyl chloride pyrolysis are SAPO-34 and SAPO-18 [20]. Many scientists have used catalysts based on copper (II) chloride in the methane oxychlorination reaction, which is explained by the relatively low cost of copper (II) chloride [21], high catalytic activity, selectivity, corrosion resistance [22]. Lanthanum chloride is used as a promoter for copper-based catalysts. Lithium or potassium is used as a catalyst enhancer [23]. Based on the above, the aim of the work is to develop a method for obtaining the catalyst \((CuCl_2) \times \cdot (KCl) y \cdot (ZnCl_2) z \cdot (MnCl_2) k\) for the process of obtaining methyl chloride by oxychlorination of methane and to study the kinetic laws of the reaction.

**Experiment.** As porous carriers, HSZ obtained from kaolin in the Pakhtachi district of the Republic of Uzbekistan was used. The catalyst was prepared as follows: 30% solution of \(CuCl_2\), \(KCl\), \(ZnCl_2\), \(MnCl_2\) was absorbed per 100 g of HSZ in 12 hours. The catalyst was then separated from the solution and dried at 350-400 \(^0\)C in a stream of nitrogen for 3 hours and reduced to a granule size of 5-7 mm. Experiments were carried out in a flow reactor under laboratory conditions. For qualitative and quantitative analysis of the products of the methane oxychlorination reaction, chromatographs LXM-80 (thermal conductivity detector) and Crystal 2000 (ionization detector) were used. The products of the methane oxychlorination reaction were analysed chromatographically under the following optimal conditions: stationary phase 15% -lestosyl on an N-AW chromaton with a particle size of 0,250-0,315 mm, a glass column with a size of 2 x 0,004 m, the temperature of the thermostat of the columns from 40 to 150 \(^0\)C, with heating at a rate of 10 \(^0\)C/min, nitrogen carrier gas flow rate of -30 ml/min [24-26].

Qualitative analysis of products was carried out by the method of "witnesses" and on the basis of structural-group components "sorbent-sorbate" system, and quantitative-method of internal normalization [27-30]. Thermal analysis of the obtained catalysts was carried out on a derivatograph Q-1500D. The porous structure of the samples was examined by low-temperature nitrogen adsorption at NOVA 1200 e. The specific surface area of the samples was calculated by BET, average mesoporous size by BJH [31-32]. After 200 hours of methane oxychlorination
reaction, the texture characteristics of the catalyst were determined. Prior to analysis of sorption properties, the samples were dried in vacuum at 250 °C.

The support (HSZ), the freshly prepared catalyst \((\text{CuCl}_2)_x\cdot (\text{KCl})_y\cdot (\text{ZnCl}_2)_z\cdot (\text{MnCl}_2)_k\) and the weight loss of the samples after several hours of use were 0.56, respectively; 2.28; and 0.90%.

**Results and discussion.** Based on the above, we investigated the catalytic activity of catalysts of various compositions based on "Zol-gel" technology in the methane oxidation reaction. The results are shown in Table 1.

**Table 1**

The catalytic activity of the methane oxychlorination reaction of catalysts of various compositions based on "Zol-gel" technology. (T=340 °C, τ=0.1sec)

| №  | Catalyst composition (in the ratio of mole) | Conversion rate, % | CH₃Cl, Selectivity, % |
|----|------------------------------------------|--------------------|----------------------|
| 1  | CuCl₂·KCl·0,3LaCl₃·SiO₂                  | 76.3               | 36.8                 |
| 2  | CuCl₂·KCl·0,3P₃3Cl₂·SiO₂                 | 80.3               | 42.5                 |
| 3  | CuCl₂·KCl·SiO₂                           | 51.6               | 28.6                 |
| 4  | ZnCl₂·KCl·HSZ                            | 49.9               | 25.4                 |
| 5  | MnCl₂·KCl·HSZ                            | 25.7               | 24.8                 |
| 6  | MnCl₂·KCl·HSZ                            | 30.6               | 30.4                 |
| 7  | CuCl₂·KCl·ZnCl₂·HSZ                      | 64.8               | 34.7                 |
| 8  | CuCl₂·KCl·MnCl₂·HSZ                      | 55.1               | 42.0                 |
| 9  | CuCl₂·KCl·ZnCl₂·MnCl₂·HSZ                | 82.6               | 44.0                 |

As can be seen from Table 1, the catalyst with \((\text{CuCl}_2)_x\cdot (\text{KCl})_y\cdot (\text{ZnCl}_2)_z\cdot (\text{MnCl}_2)_k\) based on "Zol-gel" technology showed the highest catalytic activity in the methane oxidation reaction. The conversion of hydrogen chloride, methane and oxygen in the presence of this catalyst was 82.6%, 44.0% and 61.3%, respectively, and the selectivity to methyl chloride was 98.6%.

After that, we learned about the effect of various factors on the rate of reaction of methane oxychlorination and the target methyl chloride product. The selectivity of methyl chloride formation depends on the temperature of the methane oxychlorination reaction. As the temperature increases, the selectivity of methyl chloride formation decreases, and the selectivity of methylene chloride formation increases. In the methane oxychlorination reaction in the range 315-340 °C, the formation of methane deep oxidation reaction products is increased to 315-340 °C.

The results are shown in the figure 1 below.

![Fig.1. The selectivity of methyl chloride formatting depends on the temperature of the methane oxychlorination reaction](image)
When studying the effect of the amount of oxygen, hydrogen chloride and methane in the starting mixture on the basic parameters of the methane oxychlorination reaction, the rate of formation of polychloromethanes increases with the increase in the amount of hydrogen chloride in the starting mixture. In the same case, with an increase in the oxygen concentration in the initial mixture, the combustion rate increases sharply and the selectivity of the formation of methyl chloride decreases. This shows the need to increase the amount of methane in the feed to improve the efficiency of the process. Based on the above, we propose the ratio of starting reagents $N_2:CH_4:HCl:O_2 = 5:14:2:1$. The choice of contact time for the methane oxychlorination reaction is an important factor in ensuring the selectivity of formation of the desired product. The results of the contact time selection study are shown in the table below.

**Table 2.** Effect of reactant contact time on process parameters in methane oxychlorination reaction

| Contact time, h | HCl conversion, % | CH₄ conversion, % | O₂ conversion, % | Selectivity, % |
|----------------|------------------|------------------|------------------|----------------|
| 0.03           | 20.45            | 12.56            | 15.23            | 0.14           |
| 0.03           | 24.58            | 3.72             | 14.22            | 0.08           |
| 0.10           | 82.6             | 44.00            | 61.30            | 0.99           |
| 0.30           | 60.65            | 26.03            | 43.25            | 1.94           |
| 0.30           | 61.43            | 25.53            | 38.23            | 1.64           |
| 1.00           | 75.31            | 55.74            | 72.05            | 2.03           |
| 1.79           | 97.30            | 55.83            | 89.87            | 2.46           |
| 1.79           | 94.35            | 54.74            | 88.53            | 4.61           |

When choosing contact time, we calculated the amount of chlorogenic compounds that can be formed in the value of different contact times, assuming that the formation of additional substances is one of the main factors. The results are presented in Table 3 below.

**Table 3.** The formation of chlorogenic products at different contact times ($τ/(ml\cdot kat\cdot hour)$)

| Substance name         | Contact time, second | 0.03 | 0.03 | 0.10 | 0.30 | 0.30 | 1.00 | 1.79 |
|------------------------|----------------------|------|------|------|------|------|------|------|
| XM                     | 0.5873               | 0.6636 | 0.4664 | 0.2144 | 0.1675 | 0.115 | 0.0963 |
| Ethyl chloride         | 0.0002               | 0.0002 | 0.0001 | 0.0001 | 0.0000 | 0.0000 | 0.0000 |
| Methylene chloride     | 0.0265               | 0.0326 | 0.0470 | 0.0218 | 0.0198 | 0.0170 | 0.0143 |
| 1,1-dixlorethane       | 0.0003               | 0.0002 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Chloroform             | 0.0013               | 0.0015 | 0.0028 | 0.0025 | 0.0020 | 0.0017 | 0.0013 |
| CH₂                  | 0.0000               | 0.0000 | 0.0000 | 0.0001 | 0.0001 | 0.0002 | 0.0002 |

As a result of the studies, the following optimal conditions for the reaction of oxychlorination of methane were revealed: catalyst content, $(CuCl_2)_{x} \cdot (KCl)_y \cdot (ZnCl_2)_z \cdot (MnCl_2)_k$, catalyst fraction size 0.7-1.2 mm, $P = 0.1$ MPa, gas flow rate 17.2 l/h, contact time 0.1 sec, linear flow rate 10.2 cm/s. The total flow rate of gases in the reactor remained unchanged by changing the flow rate of nitrogen. These conditions allow the reaction to proceed in the kinetic region. The influence of by-products (methylene chloride, chloroform, carbon (IV) chloride and the products of the reaction of complete oxidation of methane) was not taken into account, since under kinetic conditions the selectivity of the process over methyl chloride exceeds 95%.
Conclusion.
1. The reaction of oxchlorination of methane is investigated in the flowing reactor and the catalyst containing CuCl2•KCl•ZnCl2•MnCl2/HSZ with high activity, selectivity and efficiency are chosen.
2. The influence of various factors on the rate of the methane oxchlorination reaction in the presence of the selected catalyst and the yield of the reaction products was studied.
3. Based on the results obtained, the kinetic patterns of the reaction were tested and the following optimal conditions of the methane oxychlorination reaction were selected: (CuCl2)x•(KCl)y•(ZnCl2)z•(MnCl2)w/HSZ catalyst, T = 340°C, t = 0.1 seconds, N2:CH4:HCl:O2 = 5:14:2:1 volumetric ratio, P = 0.1 MPa, size of catalyst fractions 0.7-1.2 mm, gas flow rate 17.2 l/h, contact time 0.1, linear flow rate 10.2 cm/s. The conversion of hydrogen chloride, methane and oxygen in the presence of the selected catalyst was 82.6%, 44.0% and 61.3%, respectively, and the selectivity to methyl chloride was 98.6%.

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