
Kinetic laws of methyl chloride paralysis Process

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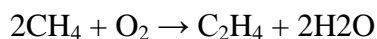
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Abstract: During the investigation, the kinetic laws of the process of obtaining ethylene and propylene by catalytic paralysis of methyl chloride obtained by oxidizing methane were studied on a catalyst 1.0% Na₄P₂O₇+1.0% B₂O₃+1.0% MgO/YuKTs. It was proved that the active life of the catalyst increases when the volumetric velocity of methyl chloride is 1000 h⁻¹. When the volumetric rate of methyl chloride is 1000 h⁻¹, the catalyst operates for 180 h with high catalytic activity, and during the experiment the activity of 1.0% Na₄P₂O₇ + 1.0% B₂O₃ + 1.0% MgO/YuKTs decreases from 89 % to 80 %.

Keywords: methyl chloride, conversion, selectivity, ethylene, propylene, volumetric velocity, temperature.

Introduction. Ethylene is the main raw material for the petrochemical industry. The most important products of ethylene processing are low and high pressure polyethylene, ethylene dichloride, ethylene oxide, ethyl benzene, and α -olefins. Low amounts of ethylene acetaldehyde are used to produce vinyl acetate, as well as a number of copolymers, including propylene, styrene, vinyl acetate, and other substances. Ethylene oligomers are the basis of a number of synthetic lubrication processes. Thus, ethylene production is of great importance for the country 's economy and the national economy. Methane oxycondensation, the MTO process, and catalytic pyrolysis of methyl chloride are currently being considered as alternative methods for obtaining ethylene. Therefore, the development of the following new processes for the production of ethylene and propylene from natural gas is of great interest:

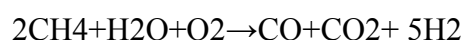
1. Methanone oxycondensate roasting [1,5,15]:



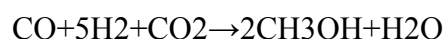
In this method, the target product (ethylene) is obtained in one step from methane. However, it has not been introduced into production due to the lack of an optimal catalytic system and reaction conditions for this process.

Extraction of ethylene from natural gas via methanol. This process consists of 3 stages [6,10, 12]:

Methane vapor and vapor-oxygen conversion:



Methanol synthesis:



Conversion of methanol to olefins:



Olefins from methanol - ethylene and propylene - are produced at UOP (USA) and Norsk Hydro (Norway) with the participation of high-yielding snake catalyst SAPO-34 (silicoalumophosphate).

1. Extraction of olefins from methane by methyl chloride synthesis and pyrolysis [11,16, 20, 21].

Obtaining methyl chloride by oxidizing methane:



production of olefins by pyrolysis of methyl chloride:



The method of obtaining alkenes by catalytic pyrolysis of methyl chloride is based on the chemical processing of methane (natural gas). In this process, methyl chloride is first obtained by oxidizing methane, and then in the second stage, methyl chloride is catalytically pyrolyzed and lower alkenes are obtained.

Among the alternative methods mentioned above, the most promising method is the conversion of methane (natural gas) to ethylene by the intermediate product methyl chloride. High-silicon zeolites currently have high catalytic activity in the production of C₂-C₄ alkenes by catalytic pyrolysis of methyl chloride [6,7,13,19].

The catalytic pyrolysis of methyl chloride of high-silicon zeolites is of great importance not only in their composition but also in the size of the pores. Typically, high-silicon zeolites with a pore size of 3.6 ÷ 4.2 Å provide selective formation of ethylene.

Numerous studies [3,4,14,17,18] have shown that when high-silicon zeolites are modified with metals such as Co, Fe, Mn, Mg, the service life of the catalyst increases, which is explained by the fact that these metals reduce the coking rate of the catalyst.

Part of the experiment. Experiments on catalytic pyrolysis of methyl chloride were carried out in a flow reactor (size of catalyst fractions 2-4 mm) process was carried out at 400-460⁰C, when the volumetric velocity of methyl chloride was 500-2500 hours⁻¹, at normal atmospheric pressure. The main products of the reaction are C₂-C₄olefins, and small amounts of C₁-C₄ alkanes are also formed as by-products. The composition of the reaction system was carried out in a capillary column filled with "Politrimethylsilylpropine" on a chromatograph "Crystal-5000.1" with a flame-ionization detector. Quantitative analysis of the released hydrogen chloride was carried out by alkalimetric titration.

Experimental results and their discussion. Catalytic pyrolysis of methyl chloride at 1.0% Na₄P₂O₇+1.0%B₂O+1.0% MgO/YuKTs was carried out in a stationary layered catalyst reactor at a volumetric rate of 1000 h⁻¹ volume of methyl chloride in the range of

temperatures 400-500°C. The results obtained are shown in Figure 1 and Table 1.

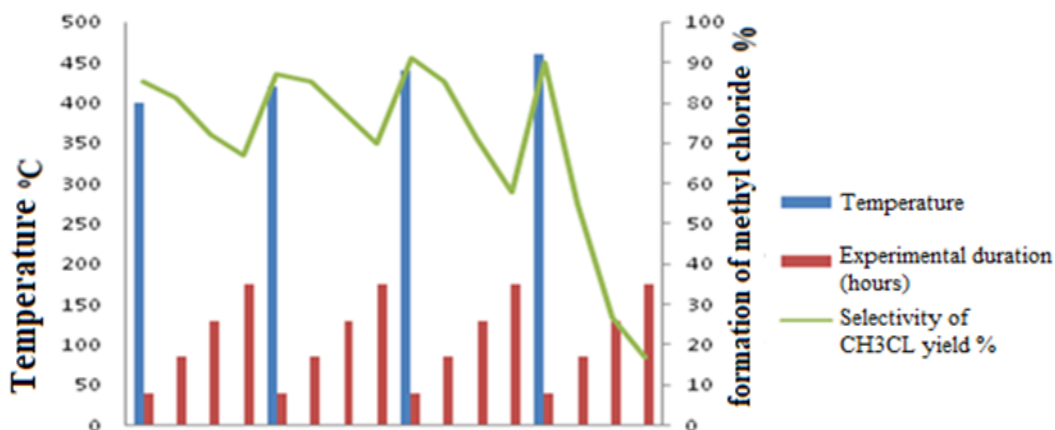


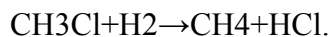
Figure 1. Changes in CH₃Cl conversion at 1%Na₄P₂O₇+1.0%B₂O₃/YuKTs at different temperatures depending on the duration of the experiment. V = 1000 hours⁻¹.

As can be seen from Figure 1, the conversion of methyl chloride in the temperature range of 400–440°C decreases with increasing experimental duration. At 460°C, methyl chloride conversion decreases from 90% to 20%. This is because as the temperature rises, more carbon-retaining layers are formed on the surface of the catalyst, and their accumulation leads to blockage of the active centers and deactivation of 1% Na₄P₂O₇ + 1.0% B₂O₃ /YuKTs.

The formation of carbon-retaining layers at the active centers of the catalyst leads to the formation of hydrogen in the products of methyl chloride pyrolysis reaction:



The hydrogen formed under the pyrolysis reaction reacts with methyl chloride to form methane:



In turn, the formation of methane leads to the formation of carbon-retaining layers and their deactivation of the catalyst. Thus, rapid deactivation of the catalyst with increasing process temperature is observed through the formation of large amounts of methane. This is the experimental data obtained fully compatible with. Experiments have shown that methane formation increases from 0.72 mol.% To ~3.60 mol.% When the temperature is increased from 400°C to 440°C. When the temperature is raised to 460°C, the selectivity of methane formation increases from 3.60 mol.% To 69.33 mol.% (Table 1).

The results of the experiments showed that the increase in the selectivity of ethylene formation in the temperature range of 400-440 °C occurs at an average of 12 mol.%.

When the process temperature is raised to 460°C, the selectivity for ethylene decreases to 29 mol.%. In the temperature range of 400-460°C, the selectivity of propylene in the reaction products decreases sharply from 51 mol.% (Table 1).

Table 1 Formation of reaction products of methyl chloride pyrolysis process temperature**effect on selectivity. Cat: 1% Na₄P₂O₇+1.0% B₂O₃/YuKTs.**

Yield selectivity, mol.%	Temperature, °C			
	400	420	440	460
CH ₄	0,7	1,1	3,6	69,3
C ₂ H ₄	29,9	34,7	41,9	28,6
C ₃ H ₆	51,3	46,6	39,8	0,0
∑C ₂ -C ₃	81,2	81,3	81,7	28,6
C ₂ +	18,1	17,6	14,7	2,1

The overall selectivity for lower olefins (ethylene, propylene) was maintained at 81 mol.% With a temperature increase in the range of 400–440 °C, an increase in the reaction temperature to 460°C led to a sharp decrease in this value to 28 mol.% (Table 1).

The laws observed at 460°C are related to the sharp increase in the formation of carbon-retaining compounds, which exactly block the active centers, thereby preventing the formation of olefins C₂-C₃ in them.

The study of the effect of volumetric velocity of methyl chloride on process parameters was carried out in a stationary catalyst bed reactor at a temperature of 440 °C at 1.0% Na₄P₂O₇+1.0% B₂O₃+1.0%MgO/YuKTs. The results of the experiments are shown in Figure 2.

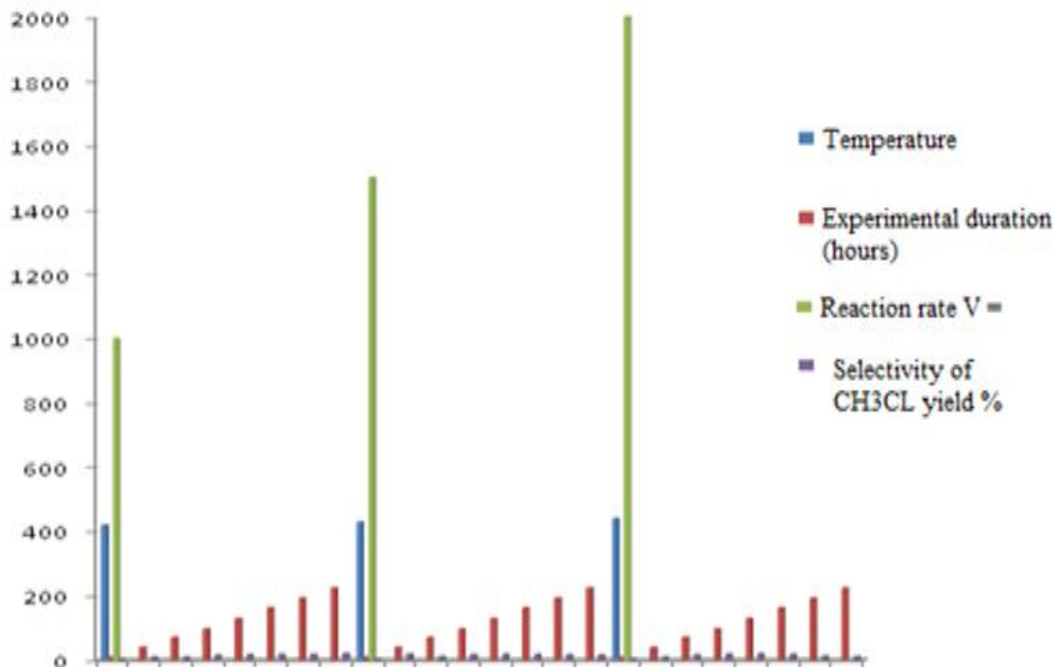


Figure 2. Change of CH₃Cl conversion at 1% Na₄P₂O₇+1.0%B₂O₃/YuKTs depending on the duration of the experiment at different volumetric velocities of the reagent. Temperature 440°C.

From the data in Figure 2, it can be seen that reducing the volumetric rate of methyl chloride to 1000 h⁻¹ allows to increase the active life of the catalyst. When the volumetric rate of methyl chloride is 1000 hours⁻¹, its activity decreases from 89% to 80% after the catalyst has

been operating for 180 hours. Doubling the volumetric rate of methyl chloride to 2000 h⁻¹ resulted in a 65% reduction in methyl chloride conversion, with no more than 35% methyl chloride conversion after 180 hours of catalyst operation.

The pyrolysis reaction obeys the kinetic equation of the first-order monomolecular reaction on the reduction of the starting material. Volumetric velocity increase in the rate of change of methyl chloride and acceleration of the formation of carbon-protective layers and their accumulation on the surface of the catalyst, which in turn leads to the activity of 1.0% Na₄P₂O₇+1.0%B₂O₃+1.0% MgO/YuKTs .

According to the results of physicochemical studies, decontamination of fresh and charcoal 1.0% Na₄P₂O₇+1.0%B₂O₃+1.0% MgO/YuKTs catalyst during methyl chloride pyrolysis was observed with a decrease in the volume of its micro-pores. In this case, a sharp decrease in the activity of 1%, 1.0% Na₄P₂O₇+1.0%B₂O₃+1.0% MgO/YuKTs when the methyl chloride volume rate is increased in the range of 1000-2000 hours⁻¹, the process of formation of carbon-protective layers and their occurs with the acceleration of the accumulation, which leads to the narrowing of the cellular channels, in which small molecules such as ethylene and propylene are now formed.

Summarizing the results of the study, it can be concluded that the increase in the temperature of the pyrolysis process of methyl chloride, as well as the volumetric load on the raw material to the catalyst

1,0%Na₄P₂O₇+1,0%B₂O₃+1,0%MgO/YuKTs

leads to a sharp deactivation of, but an increase in the selectivity of ethylene formation is observed. Defined laws

1,0%Na₄P₂O₇+1,0%B₂O₃+1,0%MgO/YuKTs

the results of the methyl chloride pyrolysis process conducted in the catalyst are well consistent with the research results.

As expected, reducing the catalyst load on methyl chloride increases its conversion, e.g., reducing the volumetric velocity of methyl chloride at 440 °C tenfold from 2400 to 440 h⁻¹ results in an increase in chloromethane conversion from 22.5% to 76% over the experimental time.

Table 2 Influence of methyl chloride volume rate on selectivity of reaction products formation in pseudodilution mode

To be harvested selectivity, mol. %	Volumetric velocity, hour ⁻¹						
	440	650	900	1152	1440	1800	2400
420°C							
CH ₄	3,3	2,7	2,6	2,7	5,9	2,3	2,7
ΣC ₂ -C ₃	68,0	77,0	78,0	79,0	76,0	82,0	84,0
^c 2+	28,0	20,0	19,0	18,0	18,0	15,0	14,0
440°C							
CH ₄	6,6	7,0	13,0	3,7	-	4,0	4,0
ΣC ₂ -C ₃	68,1	74,0	74,0	82,0	-	82,0	83,0
^c 2+	26,0	19,0	13,0	14,0	-	14,0	14,0

The reduction of the volumetric rate of methyl chloride at a temperature of 420°C from 2400 to 440 h⁻¹ resulted in a significant increase in methyl chloride conversion. At the specified

contact, methyl chloride conversion increases from 15% to 77% 180 hours after catalyst operation. An increase in temperature results in a decrease in methyl chloride volume conversion rates from 2400 to 440 h⁻¹. Thus, pyrolysis at large volumetric loads of methyl chloride is characterized by low efficiency, which leads to over consumption of the starting raw material.

The selectivity for ethylene at high 440°C is slightly higher on average 6-9 mol.% Than at 420°C. With increasing the volumetric velocity of methyl chloride from 440 to 2400 h⁻¹, the selectivity for ethylene at 420°C increases from 27 mol.% To 43 mol.%, And at 440°C its growth ranges from 33 mol. To 45 mol.%.

It was found that the dynamics of the change in the selectivity of ethylene formation in the range of 440-2400 h⁻¹ of the volumetric velocities of the raw material at both temperatures had a similar appearance.

According to the data in Table 2, increasing the volumetric velocity of methyl chloride in the temperature range 420-440°C from 440 to 2400 h⁻¹ results in an increase in olefins C₂-C₃ formation from 68 mol. To 84 mol% after 180 h of catalyst operation.

Carrying out the process of pyrolysis of methyl chloride to lower olefins under the above conditions allows to obtain industrially significant values of the main parameters of the process.

The effect of linear velocity on the main characteristics of the process for the effective conduct of the process of methyl chloride pyrolysis of 1.0%Na₄P₂O₇+1.0% B₂O₃+1.0%MgO/ YuKTs in the pseudo-dilution regime was studied.

A series of experiments were performed in which the linear velocity of methyl chloride at 1000 h⁻¹ volumetric velocity and at a temperature of 420°C was changed in the range of 1.0–7.0 cm/m. The conversion of methyl chloride to the selected linear velocity range, as well as the selectivity of formation of the main pyrolysis products, remain virtually unchanged.

Figure 2 shows the change in methyl chloride conversion depending on the contact time at different velocities of the linear velocity. It can be seen that all the points lie in the bonding solution, which confirms that the linear velocity in the selected range of 1–7 cm/m has no effect on methyl chloride conversion.

The data obtained are the basis for assuming that the selected linear velocity range (1–7 cm/m) contains acceptable values, in which the conversion rate of methyl chloride as well as the selectivity of ethylene and propylene formation are stable and acceptable.

Table 3 Influence of linear velocity on methyl chloride conversion, as well as selectivity of methyl chloride pyrolysis products

Technological indicator Linear fast	lik, cm / m.				
	1	1,5	3	5	7
Conversion CH ₃ Cl,%	61,4	65,7	63,0	64,6	62,7
CH ₄ selectivity of formation, mol.%	2,7	3,1	2,7	2,6	2,7
C ₂ H ₄ selectivity of formation, mol.%	33,8	33,9	33,6	33,1	34,0
C ₃ H ₆ selectivity of formation, mol.мол.%	43,4	42,7	43,1	41,9	42,8
∑C ₂ –C ₃ selectivity of formation, mol.%	77,3	76,6	76,7	75,0	76,8
C ₂ +selectivity of formation, mol.%	20,1	20,4	20,7	22,4	20,5

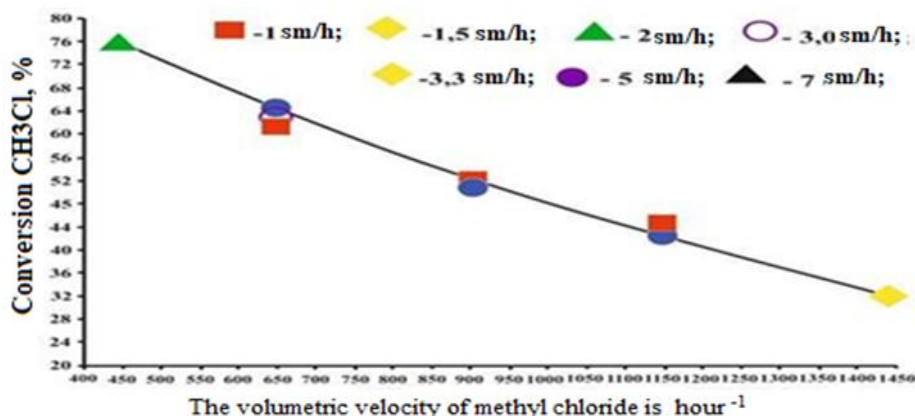


Figure 3. Dependence of CH₃Cl conversion at different linear velocities on volumetric velocity of methyl chloride delivery

High conversion of methyl chloride and high selectivity of formation of low olefins is achieved when the process of catalytic pyrolysis of methyl chloride is carried out in the pseudo-dilution mode in the temperature range 420-440°C and volumetric rate of methyl chloride 1000 h⁻¹.

A number of experiments were performed to determine the active life of the catalyst, as well as the status of the catalyst 1.0%Na₄P₂O₇+1.0% B₂O₃+1.0%MgO/YuKTs under long-term operation. The results obtained are shown in Figure 4.

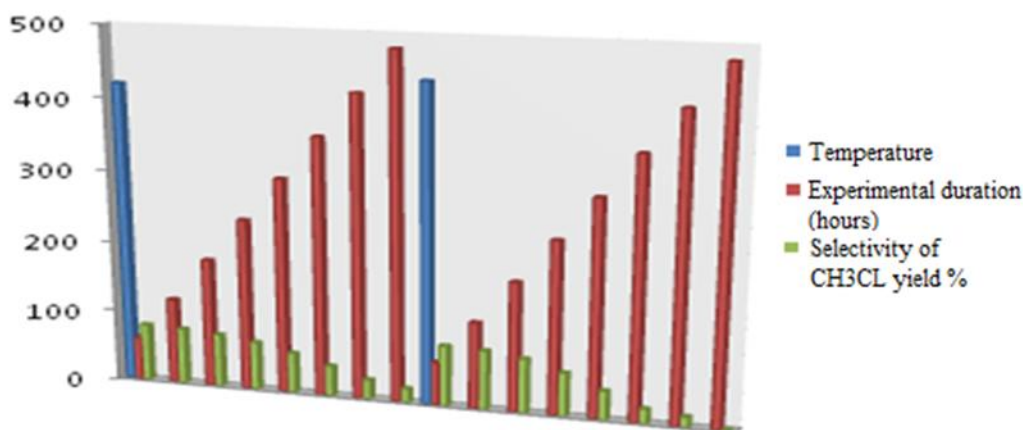


Figure 4. Changes in CH₃Cl conversion depending on the operating duration of the catalyst at different temperatures

1,0%Na₄P₂O₇+1,0%B₂O₃+1,0%MgO/YuKTs, V=1000h⁻¹

The results of a series of experiments showed that prolonged operation of the catalyst for 200 hours leads to its sharp decontamination, which in turn is caused by the formation and accumulation of carbon-retaining layers on its surface, which was confirmed by increased methane formation over time.

Conclusion. Analysis of the reaction product mixture showed that in the first 180 hours of catalyst operation, the total selectivity for C₂-C₃ olefins reaches 77-79 mol.% In the temperature range 420-440°C. Much of the catalyst common on C₂-C₃ olefins at a temperature of 420°C for 200 hours of long operation leads to a stabilization of selectivity at 79-80%. In turn, a decrease in selectivity for lower olefins from 79 mol.% To 32 mol.% Was observed with increasing the duration of the experiment to 44 h at 440°C.

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