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# INVESTIGATION OF KINETICS OF METHYLCHLORIDE PYROLYSIS PROCESS

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## ABSTRACT

*Currently, the main source of lower olefins is crude oil. However, limited oil reserves limit the possibility of increasing the production of ethylene, the demand in the market tends to constantly high growth. In this regard, the expansion of the raw material base for the production of ethylene is an urgent problem, the solution of which is to use natural gas as a feedstock for the production of ethylene.*

***Keywords:*** *methyl chloride, methyl, ethylene, lanthanum, propylene, kinetic equation, activation energy.*

## АННОТАЦИЯ

*В настоящее время основным источником низших олефинов является нефтяное сырье. Однако ограниченные запасы нефти ограничивают возможность увеличения объемов производства этилена, спрос на рынке имеет тенденцию к постоянному высокому росту. В связи с этим расширение сырьевой базы для производства этилена является актуальной проблемой, решение которой заключается в использовании природного газа в качестве сырья для получения этилена.*

***Ключевые слова:*** *метилхлорид, метил, этилен, лантан, пропилен, кинетик тенглама, активланиш энергияси.*

## INTRODUCTION

Alternative methods for producing light olefins are the production of ethylene from methylene, dimethyl ether, and methyl chloride. All listed compounds can be obtained by chemical processing of methane. The disadvantage of methods for obtaining olefins from natural gas using methanol and/or dimethyl ether is the need to convert natural gas to synthesis gas using water vapor, oxygen or carbon dioxide; the subsequent conversion of the synthesis gas to methanol and/or dimethyl ether and, finally, the third stage, the conversion of methanol and/or dimethyl ether to light olefins. The production of methyl chloride by methane oxychlorination and methyl chloride pyrolysis is convenient [4].

**DISCUSSION AND RESULTS**

The use of methyl chloride as a raw material makes it possible to reduce the process of obtaining olefins from methane to two stages:

• direct or oxidative chlorination of methane to produce methyl chloride;

• direct transfer of methyl chloride to olefins in the presence of zeolites [5].

Ethylene and propylene are obtained with high selectivity by pyrolysis of methyl chloride on a SAPO-34 silica-aluminophosphate catalyst [8]. However, there is a disadvantage associated with the fact that at least half of the chlorine used for the production of methane chloride by direct chlorination of methane is converted into hydrogen chloride. On the same catalyst [1] and at the same temperature, ethylene and propylene were obtained with a selectivity of ~85%. At this time, the conversion of methyl chloride was ~75%. The catalyst for the methane processing process is a mixture of copper, potassium and lanthanum chlorides with a molar ratio of 1: 1: 0.3, which is introduced into a porous carrier with a surface area of 1-0 $m^2$ in the amount of 3-30 wt%[6]. Previously, we produced ethylene and propylene on a catalyst containing 1.0% $Na_4P_2O_7$ + 1.0% $B_2O_3$ + 1.0% MgO / SCC in conditions V=1000 h-1, T=420 $^oC$ with a conversion of methyl chloride of 63.84%, selectivity for the formation of alkanes $\sum C_2$-$C_3$ of 89.45 mol% [17]. As a result of the research, it was found that as a result of the catalytic pyrolysis of methyl chloride, in addition to ethylene and propylene, butane and butenes, pentane and pentenes are also formed. The reactions of formation of these products can be represented as follows:

$2CH_3Cl_{(g)} \rightarrow C_2H_{4(r)} + 2HCl_{(g)} - 9{,}63$ kkal/mol

$3CH_3Cl_{(g)} \rightarrow C_3H_{6(g)} + 3HCl_{(g)} - 0{,}58$ kkal/mol

$4CH_3Cl_{(g)} \rightarrow C_4H_{8(g)} + 4HCl_{(g)} + 5{,}75$ kkal/mol

$C_5H_{10(g)} \rightarrow C_2H_{4(g)} + C_3H_{6(g)} - 35{,}81$ kkal/mol

Methyl chloride is a by-product changes and is considered lower alkanes and carbon preservative compounds that are in the catalyst:

$CH_3Cl(g) + H_2(g) \rightarrow CH_4(g) + 2HCl(g) + 19{,}31$ kkal/mol $2CH_3Cl(g) + H_2(g) \rightarrow C_2H_6(g) + 2HCl(g) + 23{,}08$ kkal/mol $3CH_3Cl(g) + H2(g) \rightarrow C_3H_8(g) + 3HCl(g) + 29{,}10$ kkal/mol $4CH_3Cl(g) + H_2(g) \rightarrow C_4H_{10}(g) + 4HCl(g) + 37{,}85$ kkal/mol

$5CH_3Cl(g) + H_2(g) \rightarrow C_5H_{10}(g) + 5HCl(g) + 42{,}13$ kkal/mol $CH_3Cl(g) \rightarrow C(kat.) + H_2(g) + HCl(g) + 1{,}43$ kkal/mol [7].

Along with the formation of alkanes and carbon-containing layers, the synthesis of higher olefins is observed, which, in turn, can undergo oligomerization with subsequent binding to the macromolecule. These compounds are the creators of

carbon-containing layers, the accumulation of which in the catalyst, in turn, leads to its disinfection [8].

$_5CH_3Cl(g) \rightarrow C_5H_{10}(g) + 5HCl(g) + 17.31$ kkal/mol

During methyl chloride pyrolysis sequential and parallel reactions occur. It should be noted that the main products are ethylene and propylene, and to simplify the methodology for conducting kinetic studies, it is desirable to represent the process of pyrolysis of methyl chloride in the catalyst

1.0% $Na_4P2O7$ + 1.0% $B_2O_3$ + 1.0% MgO / SCC through the following gross equation:

$5CH_3Cl_{(g)} \rightarrow CH_2{=}CH_{2\,(g)} + CH_3{-}CH{=}CH_{2\,(g)} + 5HCl_{(g)}$ -10,164 kkal/mol

Pyrolysis of methyl chloride to lower olefins involves a heterogeneous-homogeneous process. The peculiarity of such processes is that the kinetic laws are controlled by both diffusion and adsorption, and in intermediate cases by the laws of chemical kinetics - by their set. The determination of the limiting phase of the process allows visualizing the general form of the kinetic equations describing the reaction of pyrolysis of methyl chloride to lower olefins. It is known that if the limiting phase has a great influence on the rate of conversion of methyl chloride to hydrocarbons in the outer or inner diffusion region, the diffusion rate per unit mass of the catalyst depends on the size of the outer surface, which determines the diffusion in the pores. In this case, the diffusion rate does not play a role in limiting the rate of the chemical reaction over the entire surface of the catalyst [9].

**Experimental part.** When determining the transition zone of the methyl chloride pyrolysis process, it is important to change the linear velocity of the gas flow (methyl chloride), as well as to conduct a series of experiments with a catalyst of different sizes. Depending on the variable parameters of the conversion of methyl chloride, analysis of the results of the change made it possible to distinguish between the kinetic and diffusion fields. Experiments on catalytic pyrolysis of methyl chloride were carried out in a flow reactor (catalyst fraction size 2-4 mm) at 400-450$^0$C, space velocity of methyl chloride 1000-2400 h-1 at normal atmospheric pressure. The main reaction products are $C_1$-$C_5$ olefins, and small amounts of $C_1$-$C_5$ alkanes are also formed as by-products [10].

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