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ИССЛЕДОВАНИЕ КИНЕТИКИ ПРОЦЕССА ПИРОЛИЗА МЕТИЛХЛОРИДА

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STUDY OF KINETICS OF METHYLCHLORIDE PYROLYSIS PROCESS

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Аннотация

Процесс каталитического пиролиза хлористого метила в исследовании 1,0%$Na_4P_2O_7$+1,0%B_2O_3+1,0%MgO/ЮКЦ в присутствии катализатора 440^{0}C при температуре V_{MX}=1000 ч$^{-1}$ учились в условиях. Катализатор не изменял своей каталитической активности до 180 часов в ходе эксперимента. Однако изучалось влияние различных факторов на скорость реакции.

Ключевые слова: хлористый метил, пиролиз, этилен, пропилен, кинетическое уравнение, энергия активации.

ANNOTATION

The process of catalytic pyrolysis of methyl chloride in the study 1,0%$Na_4P_2O_7$+1,0%B_2O_3+ +1,0%MgO/ YUkts in the presence of a catalyst 440^{0}C at temperature V_{MX}=1000 h^{-1}studied under conditions. The catalyst did not change its catalytic activity up to 180 hours during the experiment. However, the influence of various factors on the reaction rate was studied.

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

Introduction

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

Alternative methods of producing light olefins are methylene, dimethyl ether, and ethylene from methyl chloride. All of the listed compounds can be obtained by chemical processing of methane.

The disadvantage of methods of producing olefins from natural gas by means of methanol and / or dimethyl ether is the need to convert natural gas into a synthesis gas using water vapor, oxygen or carbon dioxide; then the synthesis gas is converted to methanol and / or dimethyl ether, and finally, in the third stage, methanol and / or dimethyl ether is converted to light olefins.

It is convenient to produce methyl chloride by oxychlorination of methane and pyrolysis of methyl chloride [1].

The use of methyl chloride as a raw material allows to reduce the process of production of olefins from methane in two stages:

- Direct or oxidative chlorination of methane to obtain methyl chloride;
- Direct transfer of methyl chloride to olefins in the presence of zeolites.

Ethylene and propylene with high selectivity were obtained by pyrolysis of methyl chloride in a SAPO-34 silica phosphate catalyst [2]. However, there is a disadvantage associated with the conversion of at least half of the chlorine used to produce methyl chloride by direct chlorination of methane into hydrogen chloride.

Ethylene and propylene were obtained with the same catalyst [3] and at the same temperature with a selectivity of ~ 85%. At this time, the conversion of methyl chloride was ~ 75%. The catalyst of the methane processing process is a mixture of copper, potassium and lanthanum chlorides with a mole ratio of 1: 1: 0.3, which is absorbed in a porous medium with a surface area of 1-60 m2 in the amount of 3-30% by mass%.

We are ahead 1,0%$Na_4P_2O_7$+1,0%B_2O_3+1,0%MgO/YUkts in a compound catalyst, V=1000 h^{-1}, T=420°C conversion of methyl chloride under conditions 63,84 %, $\sum C_2$-C_3 we obtained ethylene and propylene under conditions of selectivity of alkanes 89.45 mol.% [4-5]

Studies have shown that in addition to ethylene and propylene, butane and butenes, pentane and pentene are also formed as a result of catalytic pyrolysis of methyl chloride.

The formation reactions of these products can be expressed as follows:

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

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

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

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

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The by-products of methyl chloride conversion are lower alkanes and carbon-retaining compounds that sit on the catalyst:

$$CH_3Cl_{(r)} + H_{2(r)} \rightarrow CH_{4(r)} + 2HCl_{(r)} + 19{,}31 \text{ kkal / mol}$$
$$2CH_3Cl_{(r)} + H_{2(r)} \rightarrow C_2H_{6(r)} + 2HCl_{(r)} + 23{,}08 \text{ kkal / mol}$$
$$3CH_3Cl_{(r)} + H_{2(r)} \rightarrow C_3H_{8(r)} + 3HCl_{(r)} + 29{,}10 \text{ kkal / mol}$$
$$4CH_3Cl_{(r)} + H_{2(r)} \rightarrow C_4H_{10(r)} + 4HCl_{(r)} + 37{,}85 \text{ kkal / mol}$$
$$5CH_3Cl_{(r)} + H_{2(r)} \rightarrow C_5H_{10(r)} + 5HCl_{(r)} + 42{,}13 \text{ kkal / mol}$$
$$CH_3Cl_{(r)} \rightarrow C_{(кат.)} + H_{2(r)} + HCl_{(r)} + 1{,}43 \text{ kkal / mol}$$

In addition to the formation of alkanes and carbon-retaining layers, the synthesis of higher olefins is observed, which in turn can undergo oligomerization with subsequent fusion of the macromolecule. These compounds are the creators of carbon-retaining layers, the accumulation of which in the catalyst, in turn, leads to its deactivation [6-13].

$$5CH_3Cl_{(r)} \rightarrow C_5H_{10(r)} + 5HCl_{(r)} + 17{,}31 \text{ kkal / mol}$$

During the pyrolysis of methyl chloride, series and parallel reactions occur. Given that the main products are ethylene and propylene, as well as to simplify the methodology of kinetic research 1,0%$Na_4P_2O_7$+1,0%B_2O_3+1,0%MgO/YUkts It is expedient to express the process of pyrolysis of methyl chloride in the catalyst by the following gross equation:

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

Pyrolysis of methyl chloride to lower olefins involves a heterogeneous-homogeneous process. The peculiarity of such processes is that the laws of kinetics are controlled by both diffusion, adsorption and in combination with the laws of chemical kinetics. Determining the limiting phase of the process allows us to visualize the general appearance of the kinetic equations describing the pyrolysis reaction of methyl chloride to the lower olefins.

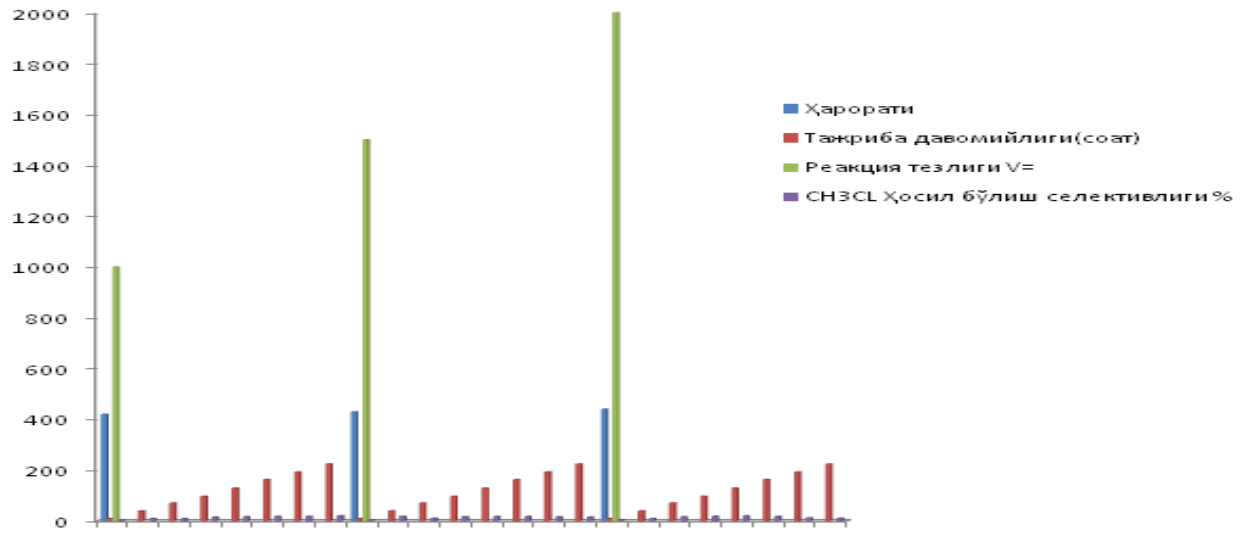
It is known that if the limiting phase has a large effect on the rate of conversion of methyl chloride to hydrocarbons in the external or internal diffusion area, the diffusion rate per unit mass of the catalyst depends on the size of the outer surface, which determines the diffusion in the pores. In this case, the diffusion rate does not play a role in limiting the rate of the chemical reaction on the entire surface of the catalyst.

Experimental Part

Investigation of the effect of volumetric velocity of methyl chloride molecules on process performance 1,0%$Na_4P_2O_7$+1,0%B_2O_3+1,0%MgO/YuKTs at 440°C at a

temperature where the stationary catalyst was held in a layered reactor. Results of experiments 1- in the picture listed.

1- in the picture the data show that reducing the volumetric velocity of methyl chloride molecules to 1000 h^{-1} allows to increase the active life of the catalyst. When the volumetric velocity of methyl chloride molecules is 1000 h^{-1}, its activity decreases from 89% to 80% after the catalyst has been operating for 180 h. Doubling the volumetric velocity of methyl chloride molecules to 2000 h^{-1} resulted in a 65% reduction in methyl chloride molecule conversion, with no conversion of methyl chloride molecules exceeding 35% 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. Increasing the volumetric velocity allows to accelerate the rate of change of reaction of methyl chloride molecules and the process of formation of carbon-retaining layers and their accumulation on the surface of the catalyst, which in turn 1,0%Na4P2O7+1,0%B2O3+1,0%MgO/YuKTs causes activity.



1-picture. 1% $Na_4P_2O_7$+1,0%B_2O_3/YuKTs changes in methyl chloride conversion depending on the duration of the experiment at different volumetric velocities of the reagent. Temperature 440°C.

According to the results of physicochemical studies, it is fresh and charcoal 1,0%$Na_4P_2O_7$+1,0%B_2O_3+1,0%MgO/YuKTs deactivation of the catalyst during the pyrolysis of methyl chloride molecules was observed with a decrease in the volume of its micro-pores. In this case, 1,0%Na4P2O7+1,0%B2O3+1,0%MgO /YuKTs A sharp decrease in the volumetric velocity of methyl chloride molecules in the range of 1000-2000 h^{-1} occurs with the acceleration of the formation of carbon-retaining layers and

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their accumulation, which leads to narrowing of cellular channels, which now contain mainly small molecules such as ethylene and propylene. is formed.

As expected, the reduction of the catalyst layer in methylide molecules increases the conversion of methylhloride, for example, 440°C The methyl chloride molecules at the temperature will increase by 2400 to 440 hours and 1,440 hours of reduction to 1 decade to increase 22.5% to 76% during the experimental period.

1- table Influence of volumetric velocity of methyl chloride molecules on the selectivity of reaction products in the dilution mode

Selection selectivity, mol.%	Volumetric speed, hours -1						
	440	650	900	1152	1440	1800	2400
420°C							
CH4	3,3	2,7	2,6	2,7	5,9	2,3	2,7
$\sum C_2 - C_3$	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							
CH4	6,6	7,0	13,0	3,7	-	4,0	4,0
$\sum C_2 - C_3$	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 molecules at a temperature of 420°C from 2400 to 440 h^{-1} resulted in a significant increase in the conversion of methyl chloride molecules. During the specified contact, the conversion of methyl chloride molecules increases from 15% to 77% after 180 hours of catalyst operation. An increase in temperature results in a decrease in the conversion of methyl chloride molecules at volumetric velocities of methyl chloride molecules between 2400 and 440 h^{-1}. Thus, pyrolysis at large volumetric loads of methyl chloride molecules is characterized by low efficiency, as it 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 an increase in the volumetric velocity of methyl chloride molecules 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 changes 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 have a similar appearance.

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