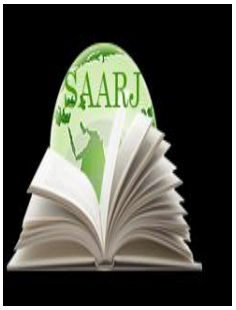

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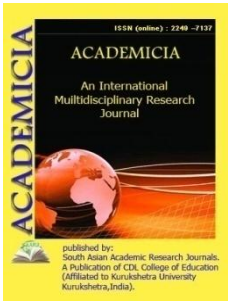

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CATALYTIC OXIDATION OF METHANE REACTION KINETICS

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ABSTRACT

The kinetic laws of the catalytic oxychlorination reaction of methane in the study (CuCl2) x · (KCl) y · (ZnCl2) z · (MnCl2) k in the catalyst, in the ratio of starting materials N2: CH4: HCl: O2 = 5: 12: 2: 1 mol , Studied at a pressure of 1 MPa. As a result of the study, the following optimal conditions for the oxidation of methane were determined: catalyst composition, (CuCl2) x (KCl) y (ZnCl2) z (MnCl2) k, size of catalyst fractions 0.7 ÷ 1.2 mm, P = 0 , 1MPa, gas flow rate 17.2 l / h, contact time 0.8 sec, linear flow rate 10.2 cm / sec. To calculate the activation energy

E_a = - (R · ln (k_ (T_1) / k_ (T_2)) · T_1 · T_2) / ((T_2-T_1))

formula was used.

KEYWORDS: *Widely, Product, Extraction, Production, And, From, Crystal, Practice, Methods, Thermal, Introduced, Selectivity*

INTRODUCTION

Ethylene is the most widely used organic substance in the world and is widely used as a starting semi-finished product in the chemical and petrochemical industries. At present, the annual demand for ethylene is 180 mln. more than a ton. To date, the following methods of ethylene production in the world practice are of great interest to scientists:

1) Extraction of ethylene by oxycondensation of methane;

2) Extraction of ethylene by methyl chloride from methane and its pyrolysis;

3) Obtaining a synthesis gas from methane and extracting methanol and ethylene from methanol.

Among the above methods, the methane catalytic oxycondensation reaction is the simplest and single-step method, which has not been introduced into the industry due to the lack of a stable

catalyst with high activity and efficiency. To date, catalysts with high catalytic activity, selectivity, and efficiency have been developed for this reaction. Such catalysts include MeMnW / SiO2 (Me = Li, Na, K) [1-3] and (MoO3) x · (ZnO) y · (ZrO2) z [4-6].

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

$2CH_4 + 2HCl + O_2 \leftrightarrow 2CH_3Cl + 2H_2O$ ΔH=157 кж/моль

$nCH_3Cl \rightarrow C_2H_4 + C_nH_{2n} + nHCl$ ΔH=-10-70 кж/моль

The main catalysts in the pyrolysis of methyl chloride are SAPO-34 and SAPO-18 [7-13].

The process of obtaining ethylene from natural gas via methanol involves the following reactions:

1) Synthesis gas extraction:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ -206 кж/моль

$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ – 247 кж/моль

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ +36 кж/моль

Part of the experiment

YuKTs from kaolin in Pakhtachi district of the Republic of Uzbekistan [15-22] were used as porous carriers in the study. The catalyst was prepared as follows: a 30% solution of CuCl2, KCl, ZnCl2, MnCl2 was injected into 100 g of YuKTs for 12 hours. The catalyst was then separated from the solution and dried at 350–4000C in a nitrogen stream for 3 h and reduced to a granule size of 5–7 mm.

Chromatographs LXM-80 (thermal detector) and Crystal 2000 (flame ionization detector) were used for the oxidation reaction of methane.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Catalysts of various compositions were prepared for the catalytic oxychlorination reaction of methane and their catalytic activity was tested. The results obtained are presented in Table 1 below.

TABLE 1 INFLUENCE OF METHANE OXYCHLORINATION REACTION PRODUCT YIELD CATALYST COMPOSITION

№	Catalyst composition (in the ratio of goods)	% акт	Conversion rate, %			CH_3Cl_2, Sselectivity
			HCl	CH_4	O_2	
1	$CuCl_2$·KCl·0,3$LaCl_3$/SiO_2	8	76,3	36,8	45,4	96,2
2	$CuCl_2$·KCl·0,3РЗЭCl_3/SiO_2	8	80,3	42,5	56,8	96,8
3	$CuCl_2$·KCl/SiO_2	8	51,6	28,6	33,4	63,8
4	$ZnCl_2$·KCl/ЮКЦ	8	49,9	25,4	26,5	62,1
5	$MnCl_2$/ЮКЦ	8	25,7	24,8	24,5	56,4
6	$MnCl_2$·KCl/ЮКЦ	8	30,6	30,4	21,2	60,2
7	$CuCl_2$·KCl· $ZnCl_2$/ЮКЦ	15	64,8	34,7	48,5	63,4

8	$CuCl_2$·KCl· $MnCl_2$/ЮКЦ		55,1	42,0	32,6	74,6
9	$CuCl_2$·KCl· $ZnCl_2$·$MnCl_2$/ЮКЦ	8	82,6	58,0	61,3	98,6

The effect of temperature on methane oxychlorination reaction The effect of temperature on methane oxidation reaction rate and product yield was studied in the range of 300-5000C. The results obtained are presented in Table 2 below.

TABLE 2 THE EFFECT OF TEMPERATURE ON THE OXYCHLORINATION REACTION OF METHANE (T = 1.5 SECONDS)

№	Temperature, ^0C	HCl conversion	CH_4conversion	O_2conversion	Selectivity,%			
					Combustion	XM	XM	
$(CuCl_2)_x$ · $(KCl)_y$ · $(ZnCl_2)_z$ · $(MnCl_2)_k$, N_2:CH_4:HCl: O_2 5:12:2:1 0,1 МПа								
30	300	15,25	1,42	18,08	0,00	100,0	100,0	0,002
31	350	59,18	5,72	48,60	1,40	98,60	93,88	0,055
32	370	75,08	13,46	59,85	4,02	95,98	89,73	0,099
33	370	80,89	8,70	67,15	5,56	94,44	89,01	0,101
34	400	92,34	12,82	76,83	7,45	92,55	86,81	0,154
35	400	89,79	12,23	74,04	7,18	92,82	87,16	0,149
36	420	95,71	19,40	78,08	10,58	96,49	84,96	0,227

The results of the study on the selection of contact time are presented in Table 3 below.

TABLE 3 INFLUENCE OF REGANET CONTACT TIME ON PROCESS PARAMETERS IN METHANE OXYCHLORINATION REACTION (N_2:CH_4:HCl:O_2 = 5:14:2:1, P=0,1 МПа, T = 380^0C)

№	Контакт вақти, с	HCl конверсияси	CH_4конверсияси	O_2 конверсияси	Селективлик,%		
					Ёниш		XM
41	0,03	0,45	2,56	15,23	0,14	99,86	97,28
42	0,03	4,58	3,72	14,22	0,08	99,92	97,06
43	0,10	29,40	6,80	31,10	0,99	99,01	94,55
44	0,30	40,65	6,03	43,25	1,94	98,06	94,06
45	0,30	41,43	5,53	38,23	1,64	98,36	90,98
46	1,00	75,31	574	72,05	2,03	98,04	92,55
47	1,79	97,30	5,83	89,87	2,46	97,54	91,40
48	1,79	94,35	4,74	88,53	4,61	95,39	90,72

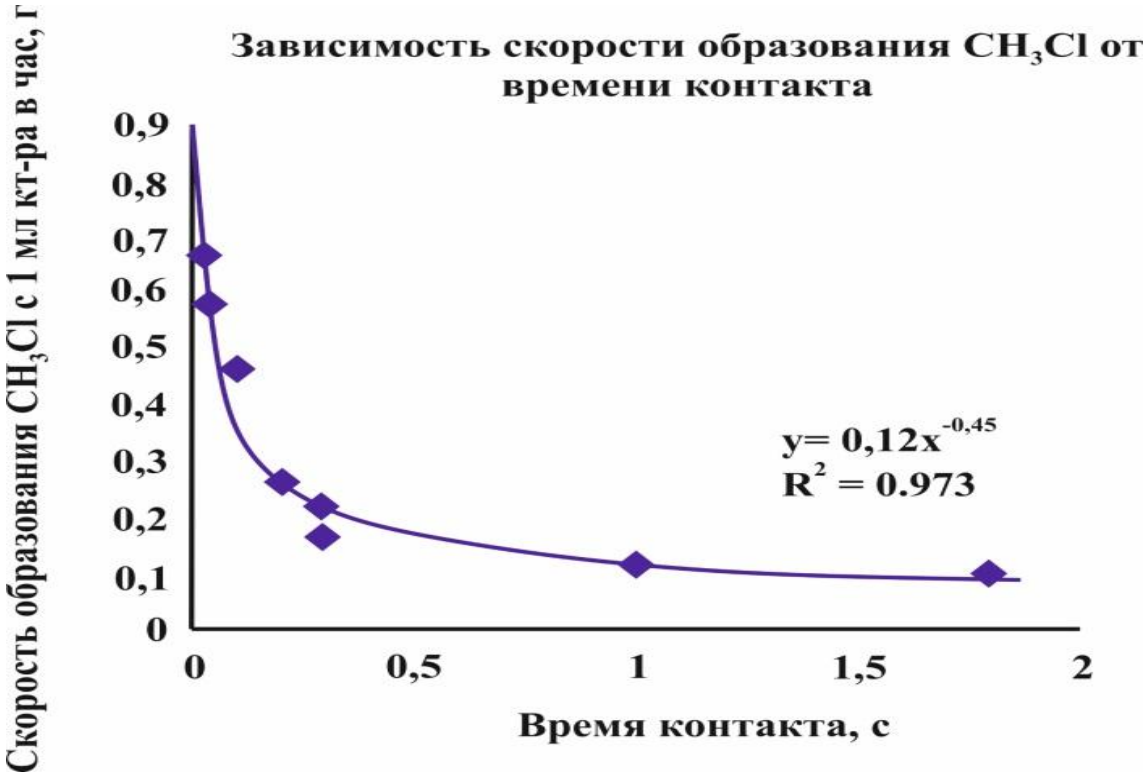
In selecting the contact time, we considered the amount of chloroorganic compounds to be formed at different contact time values, assuming that the formation of additives was one of the key factors. The results are presented in Table 4 below.

TABLE 4 FORMATION OF ORGANOCHLORINE PRODUCTS AT DIFFERENT CONTACT TIMES (T / (ML · KAT · H)

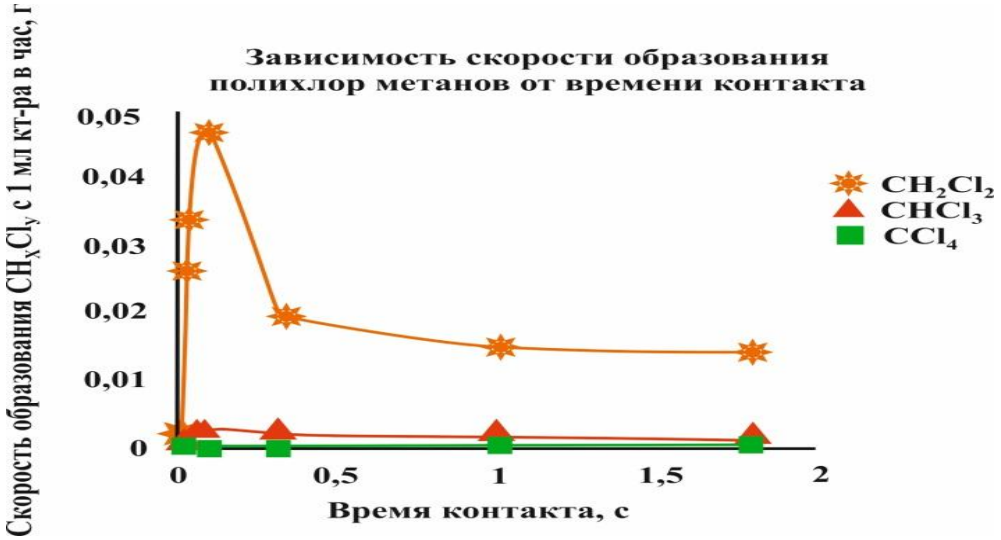
Модда номи	Контакт вақти,с							
	0,03	0,03	0,10	0,30	0,30	1,00	1,79	1,79
XM	0,587	0,663	0,464	0,214	0,167	0,115	0,0963	0,0898
Этил хлорид	0,002	0,001	0,001	0,001	0,000	0,0000	0,0000	0,0000
Метиленхлорид	0,025	0,032	0,040	0,028	0,019	0,0170	0,0143	0,0145

1,1-дихлорэтан	0,003	0,002	0,000	0,000	0,000	0,0000	0,0000	0,0000
Хлороформ	0,003	0,002	0,03	0,025	0,002	0,0017	0,0013	0,0012
ЧХУ	0,000	0,0000	0,00	0,001	0,001	0,0002	0,0002	0,0001

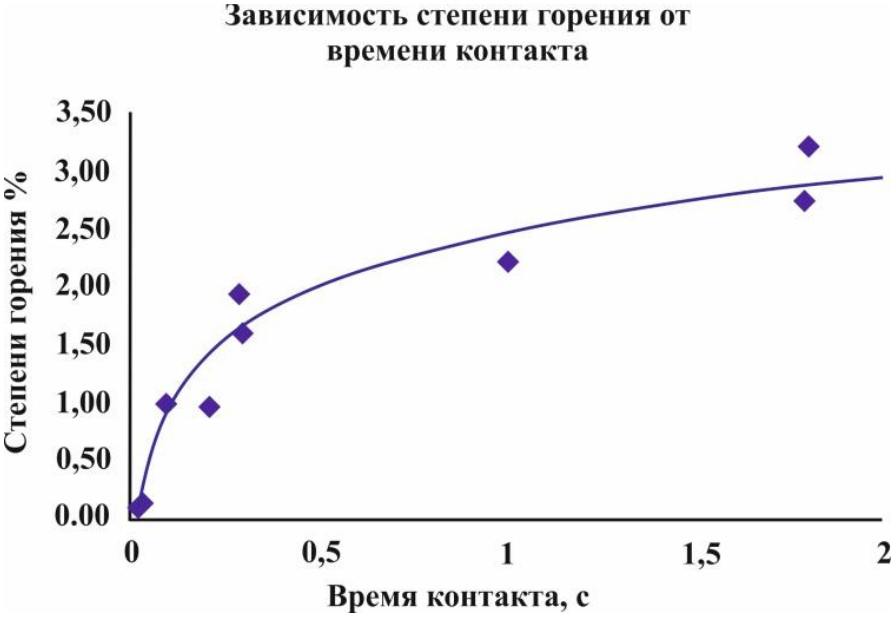
Based on the results obtained, the contact time methyl chloride (Pic. 1),



polychloromethanes (Figure 2)



and combustion products (Figure 3)



graphs of dependence were formed.

When the contact time is less than 0.3 s, the amount of methyl chloride increases as the rate and selectivity of the methane oxychlorination reaction shifts towards methyl chloride formation. This is primarily due to a decrease in the rate of combustion. Second, the smaller the contact time, the less time it takes for the methyl chloride formed in the reaction to undergo a series of reactions with the formation of methylene chloride, chloroform, and carbon (IV) chloride. As can be seen from the table, the formation of carbon (IV) chloride is not observed in the range of 0.03-0.1 sec.

Kinetic laws of methane oxychlorination reaction

As a result of the study, the following optimal conditions for the oxidation of methane were determined: catalyst composition, (CuCl2) x · (KCl) y · (ZnCl2) z · (MnCl2) k, size of catalyst fractions 0.7 ÷ 1.2 mm, P = 0 , 1MPa, gas flow rate 17.2 l / h, contact time 0.8, linear flow rate 10.2 cm / sec.

The total gas flow rate in the reactor remained unchanged due to the change in the nitrogen flow rate. These conditions ensure that the reaction takes place in the kinetic field. The effect of additional products (methylene chloride, chloroform, carbon (IV) chloride, and products of complete oxidation reaction of methane) was not taken into account, as the selectivity of the process relative to methyl chloride under kinetic conditions is higher than 95%.

To calculate the activation energy

$$E_a = -\frac{R \cdot ln\left(\frac{k_{T_1}}{k_{T_2}}\right) \cdot T_1 \cdot T_2}{(T_2 - T_1)}$$

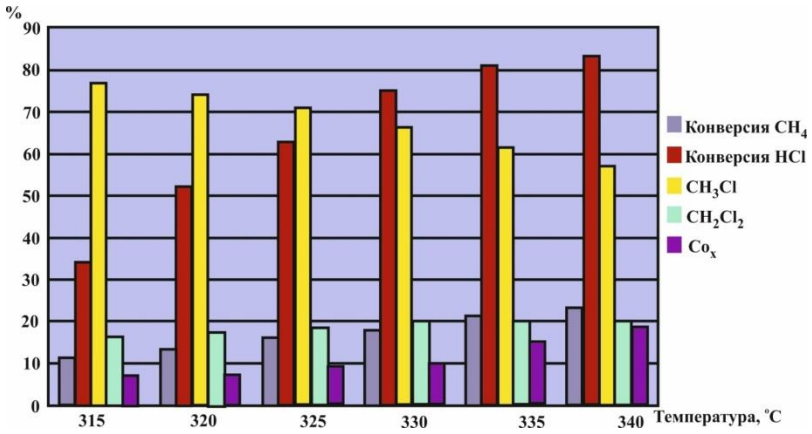
formula was used.

k_{T_1} was calculated according to the following formula:

$$k_{T_1} = \frac{R(CH_3Cl)}{P_{CH_2}^{0,7} \cdot P_{H_2O}^{0,44}}$$

We did not take into account the concentration of HCl in the calculation because its value is approximately 1. Thus, the activation energy is 96.74 kJ / mol

The selectivity of methyl chloride formation depends on the temperature at which the methane oxychlorination reaction takes place. the selectivity of methyl chloride formation decreases with increasing temperature, while the selectivity of methylene chloride formation increases. In the oxidation reaction of methane, the formation of products of the deep oxidation reaction of methane in the range of 315-3400C increases to 315-3400C. The results obtained are shown in Figure 4 below.



The texture characteristics of the catalyst were determined after 100 h of the methane oxychlorination reaction. The samples were dried in vacuum at 2500C before studying the sorption properties.

Nositel (YuKTs), a newly prepared catalyst (CuCl2) x · (KCl) y · (ZnCl2) z · (MnCl2) k, and the mass loss of samples after hours of use were 0.56, respectively; 2.28; and 0.90%.

CONCLUSION

The kinetic laws of the catalytic oxychlorination reaction of methane (CuCl2) x · (KCl) y · (ZnCl2) z · (MnCl2) k in the catalyst, the ratio of the starting materials N2: CH4: HCl: O2 = 5: 12: 2: 1 mol and 0.1 MPa was studied at pressure.

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