International Journal of Psychosocial Rehabilitation, Vol. 24, Issue 04, 2020
ISSN: 1475-7192

Kinetics and Mechanisms of Oxycondensation Reaction in Methane Molybden-Marganets-Zirconium Catalysis

N.I. Fayzullaev and Sh. B. Raxmatov

Abstract--- *Based on the ultrafine molybdenum-manganese-zirconium-containing powder, an effective catalyst has been developed for the oxidative dimerization of methane. To obtain molybdenum-manganese-zirconium-containing compounds, the sol-gel method was used. The particle sizes and chemical composition of the obtained compounds were determined. The use of the synthesized product as a catalyst allows to reduce the temperature of the reaction, the oxidative dimerization of methane and to increase the selectivity of the process. In the presence of the obtained catalyst, the kinetic laws of the oxidative dimerization of methane were studied, and a mechanism and kinetic model of the reaction were proposed on their basis.*

Keywords--- *Temperature, Bulk Velocity, Adiabatic Reactor, Contact Time, Conversion, Diameter, Film Thickness, Mass Transfer.*

I. INTRODUCTION

Limited oil resources and rising oil prices stimulate research on the production of organic products from other sources of carbon raw materials. Without underestimating the importance of coal and bioresources, it is natural gas that should be considered the closest alternative to oil in the production of products of basic organic synthesis [1-2]. Uzbekistan occupies a special place both in explored reserves of natural gas (about 5% of world reserves) and in terms of its production [2-3]. But the scale of production and production of gaseous hydrocarbons (including those of petroleum origin) significantly exceeds the share of their qualified use. Due to the irrational use of hydrocarbon gases, accompanied by their flaring, valuable chemical raw materials are irretrievably lost, and the environmental situation in the oil and gas production and processing areas is constantly deteriorating. For Uzbekistan, the qualified use of natural gas is also promising in connection with the existence of an effective gas pipeline system that allows for the guaranteed supply of gas raw materials to the places of its processing to target petrochemical products [4-5].

Among the processes of direct processing of methane into organic products, starting from the 80s, the oxidative dimerization of methane (ODM) with the formation of ethane and ethylene has been widely studied.

At the same time, it is known that methyl groups of other compounds, such as toluene, acetonitrile, etc. can also enter into the processes of oxidative condensation with methane. Systems effective in the ODM process have also been proposed as catalysts for these reactions. However, the conduct of these reactions in the presence of catalysts based on lanthanide oxides has not been sufficiently studied, although these oxides are generally recognized to be most active in ODM.

N.I. Fayzullaev, Samarkand State University, Uzbekistan.
Sh. B. Raxmatov, Bukhara Medical Institute, Uzbekistan.

DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020

The aim of this work is to study the influence of the nature of the support and texture characteristics on the activity of $Mn_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$, $(KCI)_x{\cdot}(Mn_2O_3)_y{\bullet}(ZrO_2)_z$ catalysts effective in ODM and to reveal the mechanism and kinetics process.

II. EXPERIMENTAL PART

The specific surface area of the obtained catalysts was determined by the Brunauer-Emmett-Teller (BET) method by thermal desorption of argon on a helium-argon mixture. The shape and particle size of the obtained powders were determined by transmission electron microscopy (TEM). TEM images were obtained on an EMV-100LM electron microscope with a resolution of 0.3 nm at an accelerating voltage of 100 kV.

The chemical composition of the powders was studied by electron diffraction and x-ray phase analysis methods. The diffraction pattern of accelerated electrons was obtained on a transmission electron microscope in the micro diffraction mode with sections up to 2 μm in size. To establish the identity of the samples of the catalysts, X-ray phase analysis was performed on a computer-controlled XRD-6100 apparatus (Shimadzu, Japan). CuK_α radiation (β filter, Ni, 1.54178 mode of current and tube voltage of 30 mA, 30 kV) and a constant detector rotation speed of 4 deg./min were used. in increments of 0.02 degrees. (ω / 2θ coupling), and the scanning angle varied from 4 to 80°. To calculate the interplanar distances, Tolkachev tables were used, and the relative intensity of the I / I_1 diffraction lines was determined as a percentage of the most pronounced reflection at the maximum [6-7].

The phase composition was determined by comparing the values of interplanar spacings obtained from the diffraction patterns and the corresponding intensities of diffraction maxima with the values presented in the PDF database (Powder Diffraction File) of the joint committee of standards - JCPDS (Join Committee on Powder Diffraction Standards) [8-9].

The catalytic properties of the synthesized ultrafine molybdenum-manganese-zirconium-containing powders in the oxidative methane oxidation dimerization reaction were determined in a flow unit in a differential quartz reactor flow ($P = 0.1$ MPa, $V_{cat} = 0.5$ ml ÷ 2 ml, CH_4: O2 = 2 ÷ 4 contact time 0.1 - 0.09 seconds) in the temperature range from 750 ° to 850 ° C [10-14].

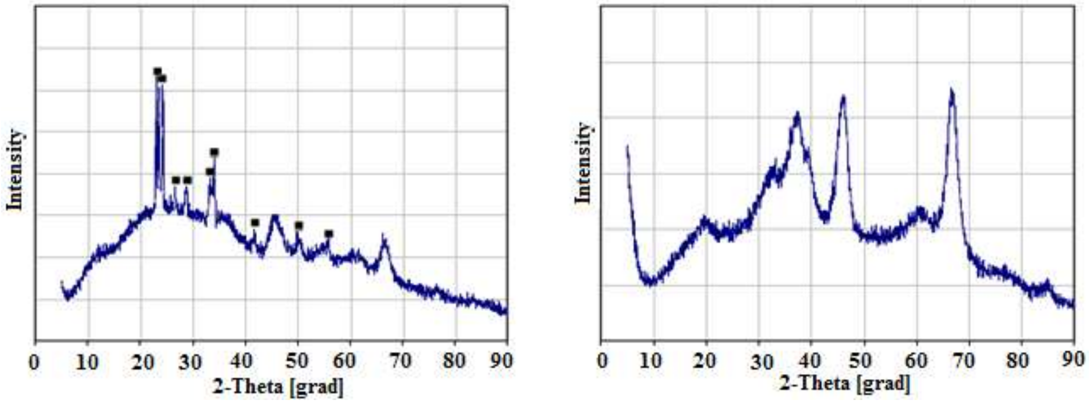
The weight of the catalyst was 0.5 g. The volumetric feed rate of the gas mixture to the catalyst was 1000 h^{-1}. The catalyst was placed in a quartz glass reactor and heated in the reaction mixture at a temperature rise rate of 4 deg / min.

The composition of the initial reaction gas mixture and the composition of the final reaction gas mixture after the reactor were determined chromatographically on a Colour-100 gas chromatograph. To determine the amount of by-products in the oxidative dimerization of methane and to determine the selectivity of the catalyst, a chromatographic analysis of the condensate was carried out on a Crystal Lux gas chromatograph [15].

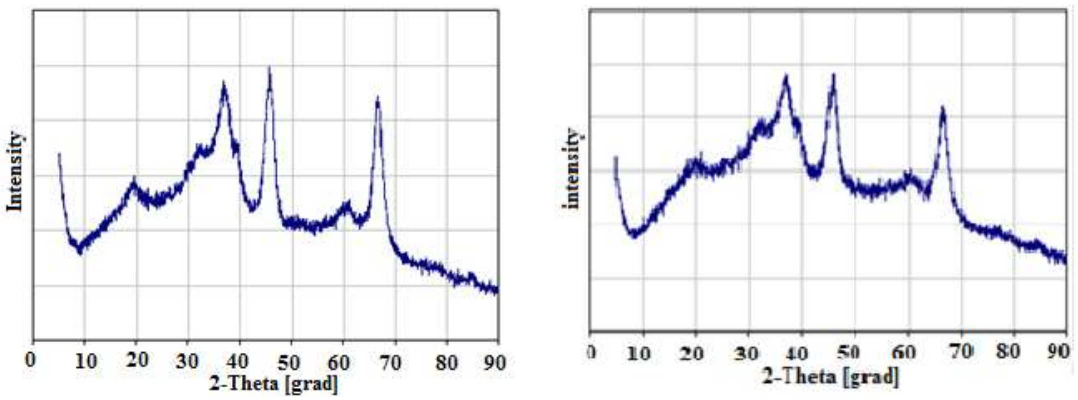
DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020

Figure 1 shows the x-ray of the obtained powder.

Mo / SKCC Mn / SKCC



Na/Mo/SKCC Na/Mn/Mo/SKCC



ZrO_2/SKCC Na/Mn/Mo/ZrO_2/SKCC

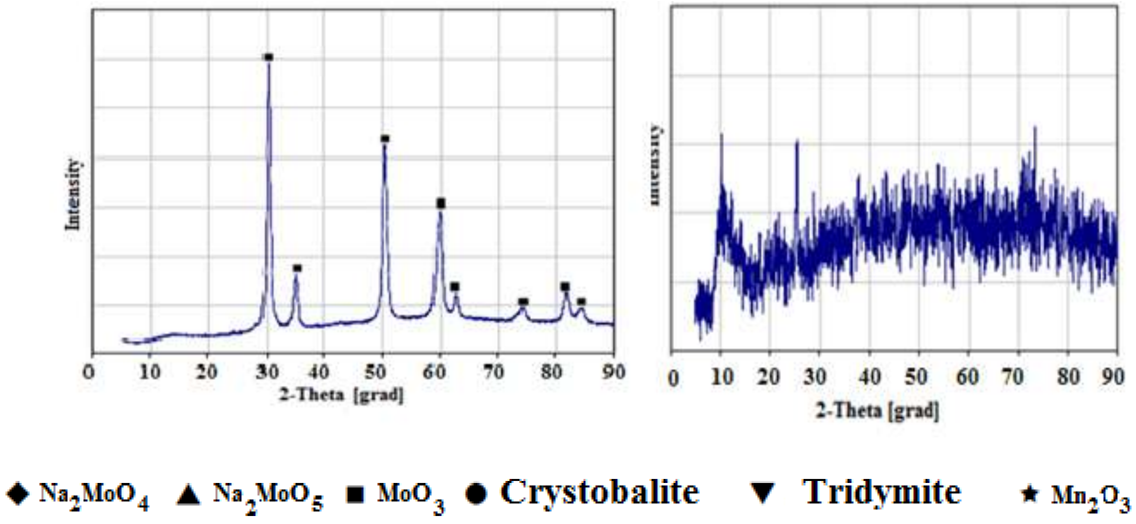


Figure 1: X-ray of Catalysts

III. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

To study the kinetic laws of the methane oxycondensation reaction, the effect of partial pressures of methane and oxygen on the rate of ethylene formation at a temperature of 700 ÷ 800^{0}C and a volumetric velocity of 600 ÷ 1200 h^{-1} was investigated.

In studying the effect of the partial pressures of the reagents on the transition laws of the process, the partial pressure of one gas was kept constant by changing the pressure of the other. The required amount of pure argon gas was sent to the reaction zone so that the linear velocity did not change. The size of the catalyst was adjusted to the research conditions to maintain a constant relative speed.

Kinetic studies have shown an improvement in process performance with increasing contact time and temperature rise.

An increase in the CH_4: O_2 ratio leads to a decrease in methane and oxygen conversion. The introduction of ethane, ethylene, CO and CO_2 into the reactor has been shown to reduce product formation. An increase in contact time leads to an increase in methane and oxygen conversion and a decrease in selectivity over ethylene. As the temperature rises, the conversion of methane increases and the selectivity for ethane and ethylene decreases. Methane: As the oxygen ratio increases, the selectivity with respect to ethane increases, while the selectivity with respect to ethylene remains unchanged.

As the temperature increases, the conversion of oxygen increases. At 700^{0}C the oxygen conversion is 95% at 0.9 s, while at 1000^{0}C the contact time is 0.009 s.

As the conversion of oxygen increases, the selectivity of the process decreases. However, this relationship with temperature is complex. As the temperature increases, the selectivity of the process decreases to 700-800^{0}C and then increases to 850-950^{0}C.

To select the experimental conditions, the methane oxidation dimerization reaction was carried out in an empty quartz reactor of different diameters (without a catalyst) and in the presence of a catalyst in the flow of a mixture of gases in different directions. The results obtained are presented in the following tables.

Table 1: Influence of Empty Reactor Volume on Product Composition in Methane Oxidation Dimerization Reaction

		V=38,3 cm^3 D = 11 mm	V = 122.8 cm^3 D = 22 mm
Conversion of methane		56.8	38.4
Conversion of oxygen		96.2	99.4
Selectivity, $S_{\%}$	C_2H_2	6.4	19.3
	C_2H_4	20.2	25.2
	C_2H_6	5.0	5.8
	CO	46.4	18.4

DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020

Table 2: Influence of the Direction of Flow of Reaction Gases on the Catalyst Activity in the Oxidative Dimerization Reaction of Methane

		Submit from below	Submit from above
Conversion of methane		58.6	61.3
Conversion of oxygen		97.2	96.8
Selectivity, $S_{\%}$	C_2H_2	6.4	4.7
	C_2H_4	21.2	16.5
	C_2H_6	3.8	2.8
	CO	20.9	40.1
Δm cat, mg		+1.3	20.4

The data show that in the methane oxidation dimerization reaction, the conversion of the starting materials and the selectivity for the products are strongly dependent on the diameter of the reactor and the direction of flow of the gas mixture.

The kinetic laws of the process of oxidation of methane in the presence of an acceptable catalyst containing $(Mn_2O_3)_x * (Na_2MoO_4)_y * (ZrO_2)_z$ were studied under differential reactor conditions at different values of partial pressures and temperatures of the starting materials and a kinetic model of the process was developed.

The kinetic equation for the catalytic oxidation dimerization reaction of methane is similar to the first-order reaction equation:

$$W = k_{ef} \cdot C_{CH_4}$$

k_{ef} - the effective constant of the reaction and represents the combination of the true rate constants of the occurrence of the elementary reactions, the development and cessation of the elementary reactions. C_{CH_4}- concentration of methane.

It is known that when using the flow method, the assumptions of the ideal compression mode are generalized and the system is considered to be in a quasi-stationary state. In this case, the following equation is appropriate for the products of the ideal squeezing regime in the reaction zone:

$$\kappa_{ef} = \frac{1}{\tau} ln \frac{1}{1-\alpha}, c^{-1}$$

where, the conversion rate of α-methane; t-contact time (ratio of the volumetric velocity of the flow through the reactor to the volume of the reactor).

The activation energy was calculated using the following equation based on experimental data obtained using the least squares method:

$$\ln k_{ef} = \ln A - \frac{E_{\alpha}^{ef}}{RT}$$

The coke formed in the methane oxidation dimerization reaction was studied using electron microscopic analysis on a scanning probe microscope (SZM Solver PRO). The results obtained by this method were also confirmed by the results of IR spectroscopy:

The kinetic and activation parameters of the methane oxidation dimerization reaction were determined by plotting the relationship between ln $\frac{1}{1-\alpha}$ and the contact time τ.

The activation energy of the methane oxidation dimerization reaction and the accumulation of ethylene and methane were found to be based on the relationship between lnk and 1 / T.

Kinetic models of methane oxycondensation reaction [16-20]:

$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$ $w_1 = k_1 \cdot P_{O_2}$

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ $w_2 = k_2 \cdot P_{O_2}$

$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$ $w_3 = k_3 \cdot P_{C_2H_6} \cdot P_{O_2}$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $w_4 = k_4 \cdot P_{CH_4} \cdot P_{O_2}$

$CH_4 + 1{,}5O_2 \rightarrow CO + 2H_2O$ $w_5 = k_5 \cdot P_{CH_4} \cdot P_{O_2}$

$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ $w_6 = k_6 \cdot P_{C_2H_4} \cdot P_{O_2}$

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ $w_7 = k_7 \cdot P_{C_2H_4} \cdot P_{O_2}$

As a result of kinetic studies and calculations, the following values of kinetic parameters were obtained:

lgk_1=24,56-18020/T; lgk_2=10,0-9997/T; lgk_3=38,72-34073/T; lgk_4 = 13,48-2855/T; lgk_5 = 18,21-6104/T; lgk_6 = 13,01-10904/T; lgk_7 = 12,87-10114/T;

where T-temperature, K.

The rate of adsorption of methane and oxygen on the catalyst surface was taken as the decisive (limiting) step in the derivation of the kinetic equation of the catalytic oxycondensation reaction of methane. The adsorption process on the surface of the catalyst is monomolecular, with methane and oxygen being adsorbed separately on the active sites.

Based on the data obtained from experimental studies, it is possible to write the basic reaction rates:

$W_1 = 0.015 \exp(-6134/T)\, C_{CH_4}^{0.4} \cdot C_{O_2}^{1.5}$

$W_2 = 0.6 \exp(-11908/T)\, C_{CH_4}^{0.8} \cdot C_{O_2}^{1.1}$

$W_3 = 1.0 \cdot 10^{-4} \exp(-772/T)\, C_{C_2H_6}^{0.8} \cdot C_{O_2}^{1.0}$

$W_4 = 1.0 \cdot 10^{-16} \exp(26461/T) C_{C_2H_4}^{0.8} \cdot C_{O_2}^{1.5}$

IV. Mechanism Of Methane Oxycondensation Reaction

It is known from the literature that the slowest step in methane activation is the disruption of the C-H bond. $CH_4 + OZ \rightarrow CH_3^{\cdot} + OHZ$ The energy barrier for the activation of the methane molecule by the reaction is ≈ 230 kJ / mol [21]. It should also be noted that the energy of activation of the methane molecule by OH · radicals is ≈ 23 kJ / mol [22]. The following is the change in Gibbs energy when activating a methane molecule with hydroxyl and hydrogen radicals:

$$\mathrm{CH_4} + \dot{\mathrm{O}}\mathrm{H} \rightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H_2O}\ \Delta\mathrm{G}^0_{298} = -64{,}3\ \mathrm{kJ}$$

$$\mathrm{CH_4} + \mathrm{H}^{\cdot} \rightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H_2}\ \Delta\mathrm{G}^0_{298} = -4{,}8\ \mathrm{kJ}$$

The calculated value of the energy of activation of the methane molecule by hydrogen radical is E_a = 40 kJ/mol [23].

Optimized intermediate state structure of methane molecule activation reactions with OH · and H · radicals (Figure 1):

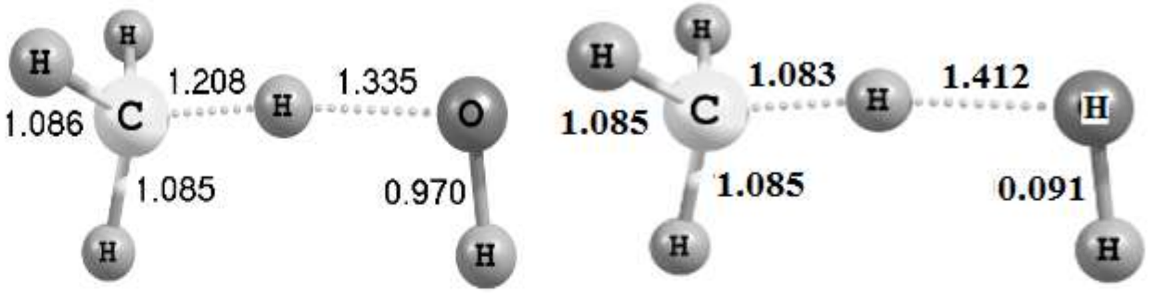


Figure 2: Optimal intermediate state structure of methane molecule activation reactions with OH · and H · radicals

The results of quantum chemical calculations of activation reactions $\mathrm{CH_4} + \dot{\mathrm{O}}\mathrm{H} \rightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H_2O}$ and $\mathrm{CH_4} + \mathrm{H}^{\cdot} \rightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H_2}$ are given in the following tables.

Table 3: The results of quantum chemical calculations of the total energy E_{total}, zero vibration energy E_0 and absolute entropy S^0_{298} for the basic and intermediate states (OH) of the molecule, as well as the reaction of activation of the methane molecule with OH-radicals $\Delta_r G^0_{298}$, $\Delta_r H^0_{298}$ and $\Delta_r S^0_{298}$ thermodynamic quantities

$$CH_4 + \dot{O}H \rightarrow H_3C - H - OH \rightarrow \dot{C}H_3 + H_2O$$

Molecular system (electron condition)	B3LYP/6-311++G(3df,3pd)			Experimental amount	
	Total energy E_{total}	Energy zero E_0 (kJ/mol)^a	S^0_{298} J/mol·К	S^0_{298} J/mol·К	$\Delta_r H^0_{298}$ kJ/mol
$CH_4(^1A_1)$ + $OH(^2\Pi)$ ↓ OX(^{2}A') Figure 1.a ↓ $CH_3\,(^2A''_2)$ + $H_2O\,(^1A_1)$ -------- $\Delta_r G^0_{298} = -52.0\ kJ$	-40.537394 -75.766245 -116.300514 $\Delta E_a = 8.2\ kJ/mol$ -39.858357 -76.464512 ----------- $\Delta_r H^0_{298} = -49.8\ kJ$	117.0(0) 22.0(0) 133.6(1) $i\omega =$ 817 cm^{-1} 78.0(0) 55.9(0)	197.5 478.2 258.2 194.3 188.6 ----- $\Delta_r S^0_{298} = +7.2\ J/К$	186.4 183.7 - 194.2 188.8 ------ $\Delta_r S^0_{298} + 12.9\ J/К$	-74.60 +38.99 - +145.7 -241.8 ------- $\Delta_r H^0_{298} = -60.5\ kJ$

DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020

Table 4: The results of quantum chemical calculations of the total energy E_{total}, zero vibration energy E_0 and absolute entropy S_{298}^0 for the basic and intermediate states (OH) of the molecule, as well as the reaction of activation of the methane molecule with H - radicals $\Delta_r G_{298}^0$, $\Delta_r H_{298}^0$ and $\Delta_r S_{298}^0$ thermodynamic quantities $CH_4 + H^{\cdot} \rightarrow H_3C - H - H \rightarrow \cdot CH_3 + H_2$

Molecular system (electronic state)	B3LYP/6-311++G(3df,3pd)			Experimental amount	
	Total energy E_{total}	Energy zero E_0 (kJ/mol)	S_{298}^0 J/mol·K	S_{298}^0 J/mol·K	$\Delta_r H_{298}^0$ kJ/mol
$CH_4(^1A_1)$	-40.537394	117.0(0)	197.5	186.4	-74.60
+					
$OH(^2P)$	-0502257	-	114.6	114.6	+218.0
↓					
$OH(^2A')$	-41.024411	111.5(1)	227.1	-	-
Figure 1.b	$\Delta E_a = 40,0\ kJ/mol$	$i\omega = 1124$ cm^{-1}			
↓					
$CH_3(^2A''_2)$	-39.858357		194.3	194.2	+145.7
+		78.0(0)			
$H_2O(^1A_1)$	-1.180034		130.25	130.5	0.0
--------	-----------	26.4 (0)	-----	------	-------
$\Delta_r G_{298}^0 = -52,0\ kJ$	$\Delta_r H_{298}^0 = -9,3kJ$		$\Delta_r S_{298}^0 = +12,4J/K$	$\Delta_r S_{298}^0 = +23,7J/К$	$\Delta_r H_{298}^0 = +2,3kJ$

The proportion of ethylene in C_2-hydrocarbons is slightly higher when halogen catalysts are used than when oxide catalysts are used. The authors [24-27] hypothesized that the dehydrogenation of C_2H_6 in the gas phase was accelerated by $Cl^{\bullet}$ radicals:

1. $H_2O^{\bullet}{\bullet}Z + 2KCl \leftrightarrow K_2O + 2HCl{\bullet}Z$
2. $HCl{\bullet}Z + OH{\bullet}Z \leftrightarrow H_2O{\bullet}Z + {}^{\bullet}Cl{\bullet}Z$
3. ${}^{\bullet}Cl{\bullet}Z+CH_4 \leftrightarrow CH_3^{\bullet}+HCl{\bullet}Z$
4. $C_2H_6+ {}^{\bullet}Cl{\bullet}Z \leftrightarrow C_2H_5^{\bullet}+HCl{\bullet}Z$
5. $C_2H_5^{\bullet}+ O^{\bullet}{\bullet}Z \rightarrow C_2H_4+HO{\bullet}Z$

where Z - the vacancy activity center of the catalyst.

In order to study the above points in more depth and to check the position of oxygen in the processes that take place, the effect of partial pressure of oxygen used as a starting material in the oxycondensation reaction of methane was studied. Initially, experiments were performed to determine the position of the oxygen involved in the reaction in the reaction mechanism.

Only methane was sent to the reactor. Experiments have shown that if the oxygen in the catalyst is not involved in the reaction, no oxycondensation will take place and the reaction products will not contain ethylene or ethane molecules. The results of the tests confirmed the presence of ethylene in the reaction products.

The results of the experiments showed that all the oxygen in the catalyst was completely consumed in the reaction of oxy-condensation. We assume that manganese oxide is the main source of oxygen in the catalyst and that it is subsequently regenerated with oxygen in the gaseous medium. Experiments were performed to modify the amount of manganese oxide in the catalyst to base this assumption. When the amount of Mn_2O_3 in the catalyst is reduced, the amount of ethylene in the reaction mixture is reduced. This assumption is proved with our point.

It is known from the literature [28-37] that the oxycondensation reaction of methane proceeds by a heterogeneous-homogeneous mechanism. Activation of methane occurs on the surface of a solid, oxidized catalyst.

At the active center of the catalyst, a single hydrogen atom is released from the methane molecule and a methyl radical is formed. Methyl radicals recombine in the gas phase to form the ethane molecule:

$$CH_4 + [O] \rightarrow CH_3^{\bullet} + [O]$$

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$$

Where [O] is the active oxygen center on the surface of the catalyst;

[OH] -hydroxy group adsorbed on the surface of the catalyst;

The process then proceeds according to the following scheme: a water molecule is formed from 2 adsorbed hydroxy groups and an oxygen void is formed on the surface of the catalyst:

$$2[OH] \rightarrow H_2O + [O] + [\ ]$$

Then the regeneration of the oxygen center takes place:

$$O_2 + 2[\ ] \rightarrow 2\,[O]$$

Dehydrogenation of ethane to form ethylene occurs at the active center on the surface of the catalyst at temperatures above 700^0C:

$$CH_4 \rightarrow [CH_3]_{ads} + 2[H]_{ads};\ 2[CH_3]_{ads} \rightarrow [C_2H_6]_{ads} + ads$$

$$[C_2H_6]_S + [O]_S \rightarrow [C_2H_5^{\bullet}]_S + [OH^{\cdot}]_S;\ [C_2H_5]_S + [O]_S \rightarrow [C_2H_4] + [OH^{\cdot}]_S$$

$$[C_2H_5^{\bullet}]_S + [O_2]_S \rightarrow [C_2H_4]+[OH^{\cdot}]_S;\ [C_2H_6]_S + [O_2]_S \rightarrow [C_2H_4]_S + 2[OH^{\cdot}]_S$$

$$[C_2H_5^{\bullet}] + CH_4 \rightarrow C_2H_6 + CH_3^{\bullet};\ [C_2H_5^{\bullet}]_S + [O_2]_S \rightarrow [C_2H_4]+[OH^{\cdot}]_S$$

$$[C_2H_6]_S + [O_2]_S \rightarrow [C_2H_4]_S + [H_2O];\ [C_2H_6]_{ads} \rightarrow [C_2H_4]_{ads} + H_2$$

The activation of methane in oxycondensation in the presence of an acceptable catalyst containing $Mn_2O_3)_x$ * $(Na_2MoO_4)_y$ * $(ZrO_2)_z$ can be expressed by the following scheme:

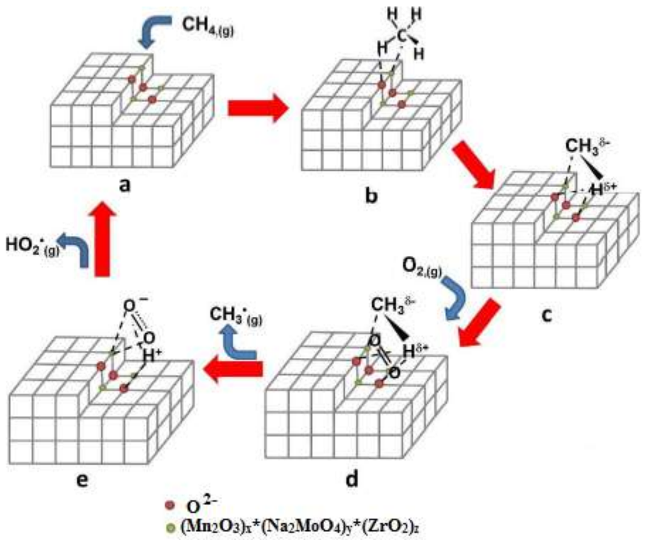


Figure 3: Activation of Methane on the Catalyst $Mn_2O_3)_x$ * $(Na_2MoO_4)_y$ * $(ZrO_2)_z$

DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020

Selective methane activation on tungstate

$$*\text{-}O*\text{-}Mo^{6+} + CH_4 \rightarrow H^+ - O * - - Mo^{6+} - CH_3^-$$

$$H^+ - O * - - Mo^{6+} - CH_3^- \rightarrow OH^{-*} + CH_3^{\cdot} + Mo^{5+}$$

$$Mo^{5+} \rightarrow Mo^{6+} + e^-$$

Redox mechanism

$$Mn^{3+} + e^- \rightarrow Mn^{2+}$$

$$Mn^{2+} + O_2 \rightarrow Mn^{3+}$$

Unselective methane activation

$$aMn_2O_3 + b\ CH_4 \rightarrow\rightarrow 2\ a\ MnO + b\ CO_x + c\ H_2O$$

Selective methane activationon manganese oxide

$$* \text{-}O * - Mn^{3+} + CH_4 \rightarrow H^+ - O* - - Mn^{3+} - CH_3^-$$

$$H^+ - O * - - Mn^{3+} - CH_3^- \rightarrow OH^{-*} + CH_3^{\cdot} + Mn^{2+}$$

V. THERMODYNAMIC ANALYSIS OF METHANE OXYCONDENSATION REACTION

The thermodynamic parameters of the reactions calculated on the basis of the values of heat and Gibbs energies are given in Table 5.

Table 5: Calculated Values of Heat and Gibbs Energies of Reactions

№	Reactions	ΔH^0_{298}; kJ/mol	ΔG^0, kJ/mol
1	$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$	-176.6	-197.296
2	$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$	-104.7	-363.242
3	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	-281.314	-280.06
4	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$	-756.162	-937.574
5	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-801.724	-1006.544
6	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	-1321.716	-1286.186
7	$CH_4 + 1{,}5O_2 \rightarrow CO + 2H_2O$	-518.738	-609.026

$\Delta_r H_0^0 = (2 \cdot (-238{,}91) + 60{,}78) - (2 \cdot (-66{,}89) + 0 = -417{,}04 + 133{,}78 = -283{,}26$ kJ/mol

900 K

$\Delta_r\left(\frac{G_T^0 - H_0^0}{T}\right) = \left(2 \cdot (-192{,}9) + (-233{,}45)\right) - (2 \cdot (-194{,}55) + (-208{,}75) = -385{,}8 - 233{,}45 + 389{,}1 - 208{,}75 = -438{,}9$

$$\ln K_T = -\frac{1}{R}\left\{\Delta_r\left(\frac{G_T^0 - H_0^0}{T}\right) + \frac{\Delta_r H_0^0}{T}\right\} = -\frac{1}{8{,}314}\left(-438{,}9 + \frac{-283260}{900}\right) = 90{,}646$$

$K = l^{lnK_r} = 2{,}33 \cdot 10^{39}$

$C_2H_6 \rightarrow C_2H_4 + H_2$ T=1000 K

$$\Delta H_r = 52{,}2 - (-84{,}7) = 136{,}9 \text{ kJ/mol}$$

$$\Delta S_r = 219{,}3 - (229{,}5 + 130{,}52) = -140{,}72 \frac{J}{mol \cdot K}$$

ΔG< 0 hence the reaction goes from a thermodynamic point of view. We find K_r:

$$\ln K_p = -\frac{\Delta G_r}{RT} = \frac{3820}{8{,}314 \cdot 1000} = 0{,}4595$$

$$K_r = e^{0{,}4595}{=}1{,}58$$

$$2CH_4 + \frac{1}{2}O_2 \leftrightarrow C_2H_6 + H_2O$$

$$(\Delta_r H^0 = -350 kj/mol\, \Delta_r G^0 = -223 kj/mol)$$

$$2CH_4 + O_2 \leftrightarrow C_2H_4 + 2H_2O$$

$$(\Delta_r H^0 = -455 kj/mol\, \Delta_r G^0 = -421 kJ/mol)$$

$$2CH_4 + \frac{1}{2}O_2 \leftrightarrow C_2H_6 + H_2O \;\; \Delta_r G^0(1000\,K) = -121{,}6\; kJ/mol$$

$$2CH_4 + O_2 \leftrightarrow C_2H_4 + 2H_2O \;\; \Delta_r G^0(1000\,K) = -152{,}5\; kJ/mol$$

VI. CONCLUSION

1. Based on the ultrafine molybdenum-manganese-zirconium-containing powder, an effective catalyst for the oxidation-dimerization of methane has been developed. To obtain molybdenum-manganese-zirconium-containing compounds, the sol-gel method was used. The particle sizes and chemical composition of the obtained compounds were determined.
2. (Mn2O3) x * (Na2MoO4) y * (ZrO2) z tarqible mabul catalyst ishtirokid methanny oxycondensation lash ryanining kinetics Kononiyatlari boshlanich moddalar partial Bosimlari va carorathning iridylaridylaridylardialyl
3. Methannic oxycondensate reaction rea son heterogeneous homogenous mechanism of Beichi ши tishi, metanning of faollanishi қatti, oxidisi catalyst of yusaside sodir bўlişi, catalysis of faol marcaside methane molecule sidanitta bitta atom atom azhralib cisilybisulisibasyl bisilybisethylbisilybisethylbisilybisulfide.
4. Methanny oksidlanishli dimerlash reaction-blueing Gibbs energy си isobland va zharayon thermodynamic zhyatatan baholandi.
5. The kinetic laws of the process of oxidation of methane in the presence of an acceptable catalyst containing $(Mn_2O_3)_x$ * $(Na_2MoO_4)_y$ * $(ZrO_2)_z$ were studied under differential reactor conditions at different values of partial pressures and temperatures of the starting materials and a kinetic model of the process was developed.
6. It has been proved that the oxycondensation reaction of methane takes place on a heterogeneous-homogeneous mechanism, the activation of methane occurs on the surface of a solid, oxidized catalyst, one hydrogen atom is released from the methane molecule at the active center of the catalyst to form methyl radicals.
7. The Gibbs energy of the methane oxidation dimerization reaction was calculated and the process was evaluated thermodynamically.

DOI: 10.37200/IJPR/V24I4/PR2020743

REFERENCES

[1] Заборовский А.М. Энергетика 2030: глобальные тренды и на-циональная энергетическая политика: моногр. / А.М. Заборовский, М.М. Ковалев, А.С. Кузнецов. — Минск : Изд. центр БГУ, 2013. – 150 с

[2] Сыркин А.М., Мовсумзаде А.М. Основы химии и переработки нефти и газа: учеб.пособ. Уфа: Изд-во УГНТУ, 2014. 148 с.

[3] Арутюнов В.С. Нефть XXI. Мифы и реальность альтернативной энергетики. М.: Алгоритм, 2016. 208. с.16.

[4] Ола Дж., Гепперт А., Прокаш С. Когда закончатся нефть и газ: пер. с англ. М.: БИНОМ. Лаборатория знаний, 2015. 416 с.18. Ергин Д. Добыча. Всемирная история борьбы за нефть, деньги и власть: пер. с англ. М.: Альпина Паблишер, 2016. 956 с.

[5] Бобохужаев Ш.И. Научный обзор: постнезависимый период развития нефтегазовой отрасли Узбекистана: успехи, проблемы и перспективы // Научное обозрение. Экономические науки. – 2016. – № 2. – С. 35-50;

[6] Синдо Д., Оикава Т. Аналитическая просвечивающая электронная микроскопия. – М.: Техносфера, 2006. – 256 с.3.

[7] Брандон Д., Каплан У. Микроструктура материалов. Методы исследования и контроля. – М.: Техносфера, 2004. – 384 с

[8] Структурные исследования [Электронный ресурс] : курс лекций /А. Д. Васильев. – Электрон.дан. (6 Мб). – Красноярск :ИПКСФУ, 2009.

[9] Zhou W.Scanning microscopy for nanotechnology: Techniques and applications / W. Zhou, Z. L. Wang –, 2007.– 1-522c.

[10] Fayzullayev N.I. Metanni katalitik oksikondensatlab etilen olish: Monografiya.dokt. texn. nauk. Samarqand, SamDU, 2019. 108-b.

[11] Fayzullayev N.I., Tursunova N.S. // Marganes saqlovchi katalizatorlarda metandan etilen olish // Kimyo va kimyo texnologiyasi. 2018. №1. C. 24-28 b.

[12] Fayzullayev N.I., Tursunova N.S., Nasimov H.M. // Metanni katalitik dimerlash reaksiyasi yordamida etilen olish.// SamDU ilmiy axborotnomasi. 2017. № 5 (105). 130-136 b.

[13] Fayzullayev N.I., Raxmatov Sh.B. // Metanni katalitik Metanni katalitik oksikondensatlash.// SamDU, Ilmiy axborotnomasi. 2018. №3 (109). 97-104 b.

[14] Fayzullayev N.I. // O‘zbekiston tabiiy gazidan etilen olishning istiqbolli usullari // Kimyo va kimyo texnologiyasi. 2014. № 4. 18-26 b.

[15] Царев Н.И., Царев В.И., Катраков И.Б. Практическая газовая хроматография. Барнаул., Изд-во Алт. Ун-та, 2000. 43 с.

[16] Fayzullayev.N.I. // Metandan etilen sintezi reaktorini modellashtirish va maqbullashtirish // SamDU ilmiy axborotnomasi. 2016. № 5. 147-153 b.

[17] Fayzullaev.N.I. // Catalytic Oxicondensation of Methane // International Journal of Chemical and Physical Science. 2015. V. 4. N 2. P. 49-54.

[18] Fayzullaev N.I., Fayzullaev O.O., Muradov K.M. // Synthesis of ethylene from methane on piled catalysts//223h National Meeting.2015. Orlando, F1.P.54.

[19] Файзуллаев Н.И., Курбанов А.М., Турдиев М.Ф. // Обобщения результатов анализа и кинетических закономерностей глобалной оптимизации реакции окислительной конденсации метана// Вестник АИНГ. 2016 г. №.4(40). С. 35-39.

[20] Fayzullaev N.I., Kurbanov A.M., Turdiev M. et al.// Global optimization of oxidative condensaion reaction of methane.// Scientific jornal of the modern education & reseach institute. The Kingdom of Belgium. 2017. V.5. P. 43-47.

[21] Experimental verification of theoretically calculated transition barriers of the reactions in a gaseous selective oxidationof CH_4-O_2-NO_2 / Tabata K., Teng Y., Yamaguchi Y. etal. // J. Phys. Chem. A. – 2000. – Vol.104. – P.2648-2654.

[22] Ogura K., Kataoka M. Photochemical conversion ofmethane // J. Molec. Catal. – 1988. – Vol.43. – P.371-379.

[23] Yan Z., Xiao C.-X., Kou Y. N Ox – catalyzed gas-phase activation of methane: in situ IR and mechanistic studies// Catal. Lett. – 2003. – Vol.85. – P.135-138.

[24] Файзуллаев Н.И. Окислительная конденсация метана кислородом воздуха// Материалы 2-го Республиканского колоквиу-ма аспирантов и докторантов Узбекистана, Ташкент, «ФАН» 1998, №3 61-63.

[25] Файзуллаев Н.И., Мурадов К.М., Сирлибоев. Т., Эгамбердиев Р. Исследование реакции окислительной конденсации метана на нанесенных катализаторах.// Узбекский химический журнал 1998, № 3 61-63.

[26] Файзуллаев Н.И. Гетерогенно-каталитическое окисление метана и цианирование спиртов// Дисс. канд. хим. наук. Ташкент. 1998. С-106.

[27] Файзуллаев Н.И., Муродов К.М., Файзуллаев О.О., Юсупов Д.Ю. Кинетика реакции окислительной конденсации метана на нанесенных оксидных катализаторах// Узб.Хим. Журнал №4, 1998 -С.33-35

[28] Ломоносов В.И., Гордиенко Ю.А., Синев М.Ю. // Кинетические закономерности окислительной конденсации метана в присутствии модельных катализаторов // Кинетика и катализ. 2013. Т. 54. № 4. С.474–486.

[29] Daneshpayeh M., Khodadadi A., Mostoufi N. et al.// Kinetic modeling of oxidative coupling of methane over Mn/Na_2WO_4/SiO_2 catalyst.//Fuel Processing Technology. 2009. Vol.90(3). № 5. P.403-410.

[30] Тюняев А.А., Нипан Г.Д., Кольцова Т. и др. // Полиморфные ОДМ-катализаторы Mn/W/Na(K,Rb,Cs)/SiO_2// Журналнеорганической химии. 2009. Т. 54. № 5. С. 723-726.

[31] Дедов А.Г., Локтев А.С., Тельпуховская Н.О. и др. // Окислительная конденсация метана в присуствии лантан-цериевых катализаторов: фундаментальный характер эффекта неаддитивности // Химия и технология топлив и масел. 2010. Т.46. №2. С.43-46.

[32] Fayzullaev N.I.,Rakhmatov Sh.B. // Kinetics and mechanism of the reaction of the catalytic oxycondensation reaction of methane.// Austrian Journal of Technical and Natural Sciences Scientific journal. 2019. №5 P. 62-69.

[33] Raxmatov Sh.B.,Fayzullayev N.I. // Metanni katalitik oksikondensatlash // SamDU ilmiy axborotnomasi. 2017. №3. 97-104 b.

[34] Fayzullayev N.I. // Metandan etilen sintezi reaktorini modellashtirish va maqbullashtirish. // SamDU ilmiy axborotnomasi. 2016. № 5. 147-153 b.

[35] Fayzullayev N.I., Raxmatov Sh.B., Norqulov U.M. // Metanni katalitik oksikondenmatlab etilen olish texnologiyasi // SamDU ilmiy axborotnomasi. 2018. №5(109). 122-129 b.

[36] Sh. B. Rakhmatov., N. I. Fayzullayev. Coke Formation of Catalyst on the Ethylene Preparation from the Oxycondensation of Methane and its Regeneration. // *International Journal of Advanced Science and Technology* Vol. 29, No. 03, (2020), pp. 7875 - 7884

[37] N. S. Tursunova, N. I. Fayzullaev. Kinetics of the Reaction of Oxidative Dimerization of Methane.// *International Journal of Control and Automation* Vol. 13, No. 2, (2020), pp. 440 – 446.

DOI: 10.37200/IJPR/V24I4/PR2020743
Received: 19 Mar 2020 | Revised: 29 Mar 2020 | Accepted: 18 Apr 2020