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Research Article

OXIDATIVE DIMERIZATION OF METHANE: KINETICS OF THE REACTION

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ABSTRACT

In this article, the textural properties of catalysts and the process of catalytic dimerization of methane using catalysts based on salts of alkali and alkaline-earth metals containing molybdenum and manganese oxides were studied. It was found that the catalytic conversion of methane takes place on the surface of a catalyst that adsorbs oxygen to form an active complex [ZOCH3]. It has been shown that the catalytic conversion of methane can be carried out simultaneously with the formation of ethane and ethylene. At the same time, the percentage of ethylene in the free volume of the reactor increases compared to ethane, which helps the reaction of ethylene formation without oxygen and catalyst. Phenomenological equations for the kinetics of the catalytic reaction of methane dimerization are formulated and rate constants and Arrhenius parameters are calculated.

KEYWORDS

Methane, ethylene, catalyst, differential reactor, X-ray, micrograph, velocity constants, Arrhenius parameters.

INTRODUCTION

One of the promising methods for producing ethylene is the reaction of oxidative dimerization of methane.

Currently, in the vast majority of cases, ethylene continues to be obtained by thermal decomposition of gasoline. However, the dynamic growth in the demand for gasoline and other motor fuels encourages the search for another innovative way to produce organic synthesis products, in particular, ethylene. Catalytic dimerization of methane, which leads to the production of ethylene, can be considered as such a method. However, this method has not yet left the scope of the laboratory experiment, which is largely due to the lack of special equipment and an adequate theoretical description of the process itself, which allows optimizing the technological regime as a whole.

A necessary condition for solving the problem is to study the kinetic regularities of the methane dimerization reaction and the thermodynamics of this process.

A number of papers [1-4] presented the results of research related to this topic, as well as proposed various catalysts for the conversion of methane to ethane and ethylene. The specificity of the methane oxidative condensation reaction is that with all known catalysts, the reaction occurs at high temperatures, and the process is highly exothermic. At the same time, the gas mixture of methane and oxygen in a wide range of their concentrations is particularly explosive.

Kinetic processes of dimerization of methane in order to obtain the target product –ethylene, even using such effective catalysts as Bi_2O_3; 9% K_2CO_3/Al_2O_3; 34% PbO/Al_2O_3; 4% $Na_2MoO_4 \cdot 10\%$ $Mn\text{-}O/SiO_2$, have not been sufficiently studied and require additional research [5-6].

Previously, we found [7-15] that the catalysts of the methane dimerization reaction containing Mn, Mo, Zr and oxides of rare earth elements have a high catalytic activity.

In this regard, the purpose of this work is to further study the influence of physical-chemical and textural characteristics on the activity of the catalyst of the composition $(Mo_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$ in the reaction of oxidative dimerization of methane and to establish appropriate kinetic models.

EXPERIMENTAL PART

The catalytic activity was studied in the differential flow of a quartz reactor ($P=0.1$ MPa, $V_{cat}=0.5$ ml$\div$2ml, CH_4: $O_2=2 \div 4$ contact time 0.1-0.09 seconds) in the temperature range from 750º to 850ºC.

The phase composition of the samples was determined by X-ray phase analysis (XRF) on a Bruker D8 diffractometer (Germany) using CuK_α

radiation (λ = 1.5418 Å) when scanning at points with an interval of 0.05° in the range 2θ from 20 to 80°. The stability of the phase composition at high temperatures (up to 900°C) was studied using high-temperature RF in the HTK-16 X-ray chamber (Anton Paar, Austria). Experiments were carried out in the air. The textural characteristics of the samples were studied using N_2 adsorption isotherms at a temperature of -196°C at the ASAP-2400 facility (Micromeritics, USA).

The morphology of the catalysts was studied using vector electron microscopy (ZEM) by Vegall LMU (Czech Republic). The porous structure was corrected based on the analysis of the obtained adsorption curves by the nitrogen thermosorption method. The specific surface area S_{spec} of the catalyst was determined by the BET method, and the volume of micro-and meso-porosity was determined by the BJH method[16].

Analysis of the gas mixture at the inlet and outlet of the reactor was performed using the gas chromatographic method [17-19].

RESULTS AND DISCUSSION

Considering the catalytic processes, it should be noted that a non-additive synergistic effect can be observed when other elements are combined as a promoter in a single system. To study the nature of this effect, the physicochemical, textural, and structural characteristics of the catalysts were studied.

According to the results of powder XRD, when active components are added to the catalyst, solid solutions containing defective oxygen voids are formed, which causes an increase in the catalytic activity of the system [20-23].

Another reason for the increase in the catalytic activity of the system is an increase in the proportion of amorphous mesoporicity.

Mesoporous amorphous catalytic systems containing Mn and Mo were obtained by the method of sol-gel - synthesis of the catalyst $(Mo_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$.

Figure 1 shows an XRD spectrum of mesoporous amorphous catalyst of the composition $(Mo_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$.

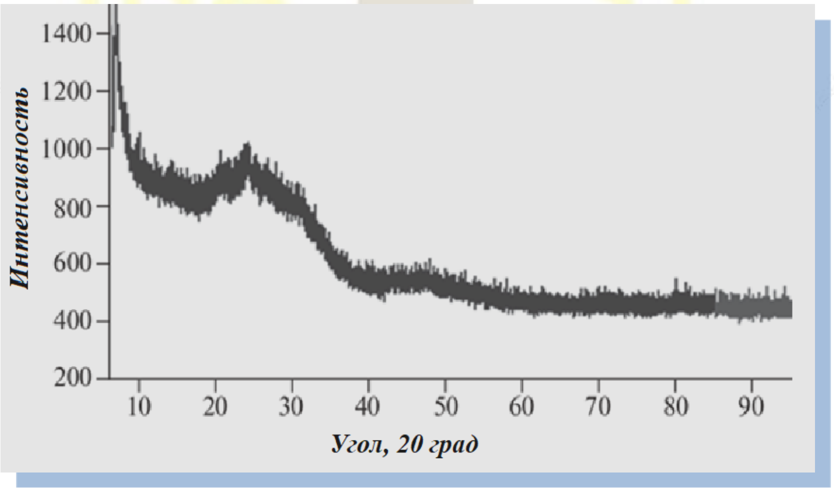

Figure 1. XRD spectrum amorphous catalyst composition $(Mo_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$

The diffractogram of a mesoporous amorphous catalyst with the composition $(Mo_2O_3)_x{\cdot}(Na_2MoO_4)_y{\cdot}(ZrO_2)_z$ agrees with the theoretical radiographs calculated from the results of XRD analysis.

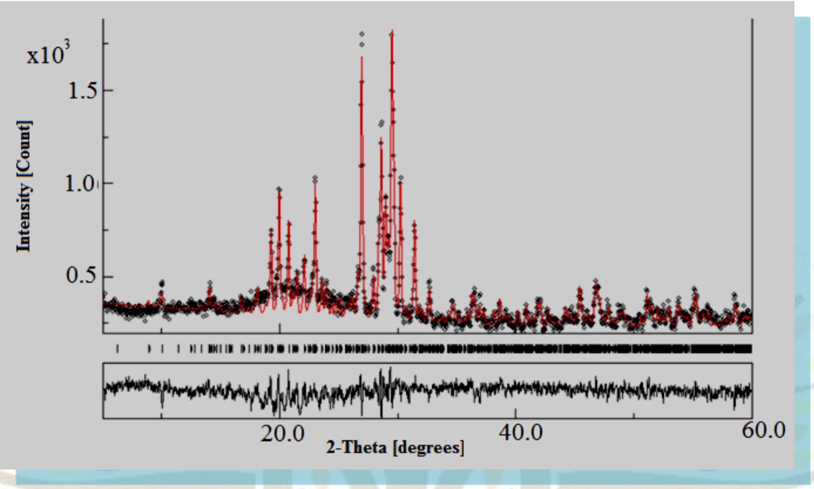

Figure 2. Experimental diffractogram of the burned (black, bottom) and calculated from the structure data (top) of the catalyst composition $(Mo_2O_3)_x{\cdot}(Na_2MoO_4)_y{\cdot}(ZrO_2)_z$

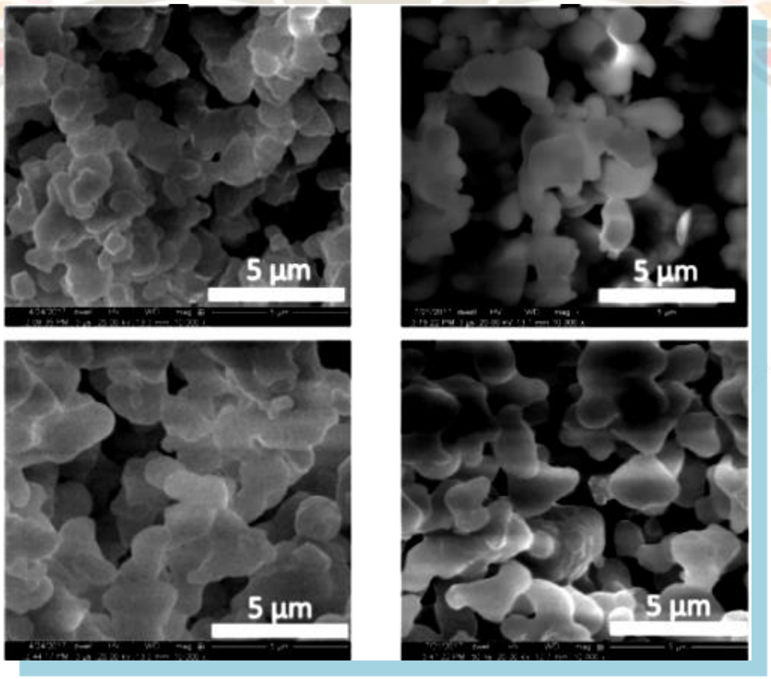

Figure 3. SEM micrograph of the catalyst $(Mo_2O_3)_x{\cdot}(Na_2MoO_4)_y{\cdot}(ZrO_2)_z$

To establish the kinetic regularities of the catalytic conversion of CH_4 to C_2-hydrocarbons, the content of ethylene and ethane in the gas mixture at the reactor outlet was quantitatively determined using catalysts of different compositions. Based on the obtained data, the catalytic efficiency of the catalyst and the conversion of methane were evaluated.

It is proved that the greatest catalytic activity, manifested in the efficiency of methane conversion, was shown by the proposed catalyst of the composition $(Mo_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$. When CO_2 is introduced into the CH_4:O_2: CO_2 system at molar ratios of the mixture components from 3:1: 0 to 3:1:2 moles, respectively, the conversion of methane increases from 52.6% to 63.1%, the selectivity increases with respect to ethylene from 62.4% to 66.2%, with respect to ethane, the selectivity increases from 19% to 20.7%; with respect to hydrocarbon C_2, the selectivity increases from 81.4% to 86.9%.

Table 1. Effect of carbon dioxide on the reaction of catalytic dimerization of methane and the yield of the target product

CH_4:O_2:CO_2	*Conversion (%)*		*Selectivity (%)*				
	CH_4	CO_2	H_2	CO_2	CO	C_2H_4	C_2H_6
3:1:0	52,6	-	6,2	13,4	16,8	62,4	19,0
3:1:1	57,2	-33,2	1,9	7,6	20,6	64,0	19,8
3:1:2	63,1	-14,0	2,6	4,1	21,0	66,2	20,7
3:1:2.5	57,1	-9,6	2,7	10,0	26,5	55,9	17,6
3:1:2.8	44,7	-1,6	3,3	3,1	70,4	45,0	11,5
3:1:3	42,7	2,0	3,1	-	92,6	32,2	5,2

As can be seen from table 1, the conversion of methane in the absence of CO_2 is 52.6%, and the selectivity for ethylene is 62.4%.

A further increase in the amount of CO_2 leads to a decrease in the above values, and the selectivity increases slightly in relation to carbon monoxide.

Under constant conditions of the experiment, but when replacing carbon dioxide with argon along with the growth of the latter, there is a decrease in the yield of C_2-hydrocarbons decreases.

Table 2. Effect of argon on the yield of the target product

CH_4:O_2:Ar	*CH_4*	*Selectivity (%)*				
		CO_2	H_2	CO	C_2H_4	C_2H_6
3:1:0	52,6	13,4	6,2	16,8	52,4	19,0
3:1:1	56,5	16,1	5,6	17,2	50,5	17,5

3:1:2	55,5	17,1	7,1	19,5	48,1	17,3
3:1:3	29,7	18,7	9,4	22,3	45,8	15,5
3:1:4	12,5	28,2	18,6	26,4	33,9	7,7

The dependence of oxygen conversion on contact time and temperature in the methane dimerization reaction with $(Mo_2O_3)_x\cdot(Na_2MoO_4)_y\cdot(ZrO_2)_z$ catalysis was investigated. The effect of temperature on oxygen conversion at a volume ratio of CH_4: air = 2:1 was studied at temperatures of 700-800°C and a pressure of P = 0.1 MPa

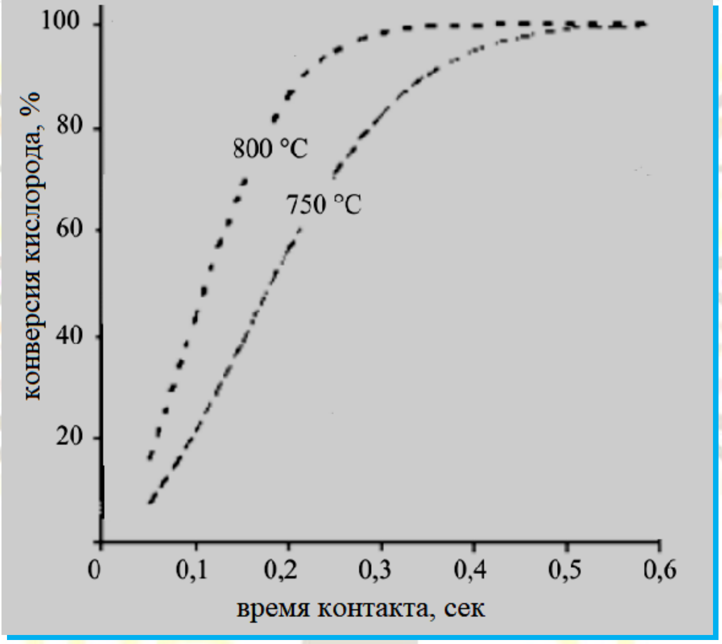

Figure 4. The relationship between the reactant contact time and the oxygen conversion temperature at the CH_4:air ratio=2:1 and a pressure of 0.1 MPa.

As can be seen from the figure, deep oxygen conversion is achieved at 750 ºC in 0.6 seconds, and at 800ºC in 0.3 seconds.

When studying the effect of pressure on the ratio of reagents, the selectivity of the ethane-ethylene mixture decreases with increasing pressure.

When the volume ratios of reagents increase, the selectivity of the process increases slightly. Thus, in the case of a 2:1 ratio of reagents, the minimum selectivity is 56.4%, and in the case of a 6:1 ratio, the selectivity reaches 76.2%.

To determine the activation energy of the process in different temperature ranges, the least square method was used. Methane conversion and selectivity of C_2 hydrocarbons were calculated using the obtained kinetic parameters.

Table 3. Arrhenius parameters calculated on the

basis of kinetic regularities of the methane dimerization reaction and experimental data

№	*Reaction of the equation*	*Kinetic equation*	*E_a, kJ/mol*
1	$2CH_4+1/2O_2 \rightarrow C_2H_6+H_2O$	$W_1=k_1\cdot P_{CH_4}^2\cdot P_{O_2}$	49,86
2	$C_2H_6+1/2O_2\rightarrow C_2H_4+H_2O$	$W_2=k_2\cdot P_{C_2H_6}\cdot P_{O_2}$	41,42
3	$2CH_4+O_2\rightarrow C_2H_4+2H_2O$	$W_3=k_3\cdot P_{CH_4}\cdot P_{O_2}$	51,35
4	$C_2H_6\rightarrow C_2H_4+H_2$	$W_4=k_4\cdot P_{C_2H_6}$	41,46
5	$CH_4+2O_2\rightarrow CO_2+2H_2O$	$W_5=k_5\cdot P_{CH_4}\cdot P_{O_2}$	44,85
6	$C_2H_4+2O_2\rightarrow 2CO+2H_2O$	$W_6=k_6\cdot P_{C_2H_4}\cdot P_{O_2}$	71,45
7	$CH_4+O_2\rightarrow CO+H_2O+H_2$	$W_7=k_7\cdot P_{CH_4}\cdot P_{O_2}$	92,11
8	$C_2H_4+2H_2O\rightarrow 2CO+4H_2$	$W_8=k_8\cdot P_{C_2H_4}\cdot P_{H_2O}$	74,6
9	$CO_2+H_2\rightarrow CO+4H_2O$	$W_9=k_9\cdot P_{CO_2}\cdot P_{H_2}$	26,47
10	$C_2H_4+3O_2\rightarrow 2CO_2+2H_2O$	$W_{10}=k_{10}\cdot P_{C_2H_4}\cdot P_{O_2}$	57,59
11	$2CO+O_2\rightarrow 2CO_2$	$W_{11}=k_{11}\cdot P_{CO}\cdot P_{O_2}$	27,23
12	$C_2H_6+2H_2O\rightarrow 2CO+5H_2$	$W_{12}=k_{12}\cdot P_{C_2H_6}\cdot P_{H_2O}$	74,6

As can be seen from table 3, the formation of ethane from methane in relation to methane is a 2nd-order reaction (see reaction 1).

CONCLUSIONS

1. The textural characteristics of catalysts and the process of catalytic dimerization of methane using catalysts based on salts of alkaline and alkaline-earth metals containing molybdenum and manganese oxides in their composition are studied.
2. It is shown that the catalytic conversion of methane can be accompanied by both the formation of ethane and ethylene. At the same time, the proportion of ethylene in the free volume of the reactor increases in comparison with ethane, which allows the ethylene formation reaction to proceed without oxygen and a catalyst.
3. Optimization of the catalytic process of dimerization of methane was performed, showing that the process should proceed at a temperature of 750-800ºC at a controlled rate of supply of the reaction mixture of gases to the reaction zone of the catalyst of 0.3 mol/sec CH_4 and 0.12 mol/sec O_2.
4. Phenomenological equations for the kinetics of the catalytic reaction of methane dimerization are built and the rate constants and Arrhenius parameters are calculated.

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