**Methane Oxidative Condensation Process Catalysts and Reaction Parameters**

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**Abstract.** In this study, the laboratory parameters of the ethane and ethylene production reaction were studied using catalytic oxidative condensation of methane, the main component of natural gas. The catalyst takes as its starting point pure methane (99.99 percent) and air containing more oxygen than atmospheric air. The experiments were carried out at temperatures ranging from 600 to 900 °C, under atmospheric pressure and at a rate approaching 1000 h-1. The catalyst active materials were Mn2O3·Na2MoO4·ZrO2. They were bound to various supports such as SiO2, Al2O3, and high silica zeolite (HSZ). At 750 °C, the methane conversion was 52.6% and the selectivity was 81,4%. Using physicochemical analyses based on IR spectroscopy, the Si-O and Mn-O bonds on the catalyst surface and the vibrational frequencies indicating the influence of adsorbed water molecules were determined. A zeolite adsorber was used to collect the mixture of products formed during the process. The mixture was desorbed by heating at 350 °C. Gas chromatography was used to determine the amounts of C2H4, C2H6, CH4, and H2, and selectivity indices were determined. The results show that changing the structure and material-thermal parameters of the catalyst can greatly increase the amount of ethylene and ethane that can be made from methane and also improve selectivity. This research is important in finding more cost-effective and environmentally friendly ways to directly convert methane into useful hydrocarbons.

**Keywords:**methane, ethane, ethylene, catalyst, reactor, mechanism, contact time, dimerization.

**INTRODUCTION**

When atmospheric oxygen undergoes oxidative condensation of methane at high temperatures (600–900 °C), ethane and ethylene are produced as the main products, with carbon monoxide (CO2) and other higher oxidation products appearing in alternative reaction pathways [1, 2]. Numerous studies on the properties of catalytic systems and the investigation of reaction mechanisms indicate that many oxide-based compounds can be good catalysts.These include intermediate metal oxides modified with alkali metal ions [3], rare earth metal oxides, and alkaline-earth and rare earth metal oxides [4–6]. At the same time, systems based on manganese oxides are also characterized by high activity and selectivity [7–9].

From the point of view of economic and technological efficiency, catalytic systems that allow the reaction to be carried out at relatively low temperatures (<800 °C) are considered the most promising. Catalysts that are effective under these conditions are usually based on mixed compounds of alkaline-earth and rare-earth elements. They often contain La2O3, which is used modified with alkaline-earth metal ions such as Cr, Mg, and Ba [10–12].

In particular, materials synthesized based on Cr and La2O3 are of great scientific and practical interest. Studies show that these compounds have high activity in the process of oxidative condensation of methane in the presence of air oxygen, and can maintain a high selectivity of the target products [13-17]. This increases the possibility of using them on an industrial scale and creates a basis for recommending them as an economically acceptable option.

The oxidative condensation reaction of methane in the presence of atmospheric oxygen has the potential to develop and become a competitive technology to meet, at least partially, the ever-increasing demand for ethylene production [1-3]. This has prompted many researchers to study various aspects of this emerging technology over the past four decades [4, 5].

Ethylene is one of the main organic synthesis products of strategic importance in the global chemical industry. It is used not only in the production of plastic and polymer materials, but also as an important intermediate reagent for the synthesis of other submolecular and liquid organic compounds derived from polyunsaturated hydrocarbons [1, 2]. Ethylene series hydrocarbons can then be converted through various conversion processes into energy-rich fractions used as fuels, particularly aviation and motor kerosenes [3, 4].

In recent years, oil prices on the world market have been growing faster than natural gas prices, and forecasts indicate that this trend will continue in the coming years [5, 6]. These factors motivated the development of the concept of "fuel switching". The main goal of this concept is to diversify the base of raw materials for the synthesis of lower molecular weight ethylene series hydrocarbons and reduce the high dependence on oil [7, 8].

The commissioning of large-scale shale gas fields, as well as the increased use of biogas sources, has created sufficient access to natural gas reserves. This has greatly increased the interest in using methane as the main raw material in chemical synthesis processes, including the production of ethylene. [10, 11].

Steam cracking and high-temperature thermal cracking are currently used as the main industrial methods of ethylene production. These technologies provide a large portion of global ethylene production. [13]. However, their high energy requirements and disadvantages in terms of environmental sustainability are one of the important problems [18–22].

There are also indirect routes to ethylene production, such as producing synthesis gas (CO/H2) from natural gas and then converting it to C2⁺ compounds via the catalytic Fischer–Tropsch process [16]. However, the first step of this technology requires the complete cleavage of the four strong C–H bonds in methane, which reduces the possibility of directly generating or radicals and increases the overall energy consumption of the process [6].

Therefore, over the past thirty years, active scientific research has been conducted to develop simple, economically viable, and environmentally sustainable alternative methods for ethylene production. [14]. One of the most promising directions is the direct production of ethane and ethylene through oxidative condensation (OC) of methane in the presence of atmospheric oxygen. This method not only reduces the environmental impact, but can also be competitive in terms of energy efficiency and economic profitability [15].

The process of oxidative condensation of methane was first intensively studied in the 1980s [14]. Scientific research is mainly focused on determining the effect of catalyst composition, modification methods and reaction parameters on conversion and selectivity. For example, it has been found that modification of CaO with alkali metals (Li–CaO, Na–CaO, K–CaO, Pb–CaO, Cs–CaO) significantly increases the formation of C2 products compared to single-component oxides. [14]. Among CaO modified with alkali metals, Li–CaO, Na–CaO, and K–CaO exhibit high catalytic activity and selectivity [15].

The Mn–Na2WO4/HSZ catalyst is also recognized as one of the most effective systems for the oxidative condensation of methane in the presence of atmospheric oxygen. This catalyst has been found to have stable activity under long-term operating conditions, with methane conversion of 20–30% and combined ethane and ethylene yields of 70–80% [16-23].

**EXPERIMENTAL PART**

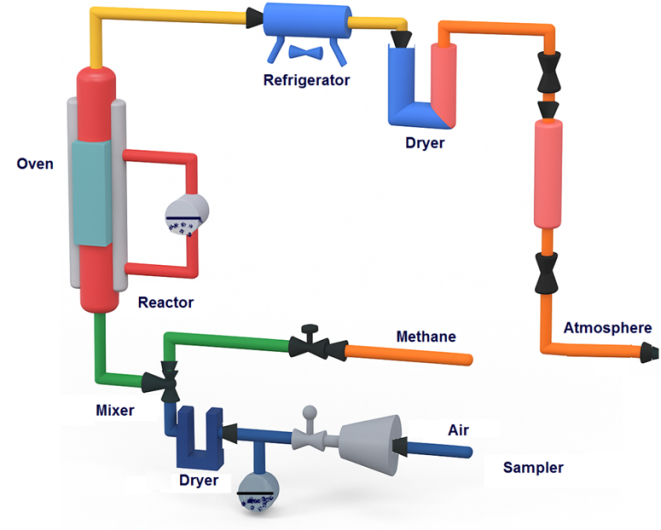
For the oxidative condensation of methane to ethylene reaction, methane (purity 99.99% by volume) and atmospheric air enriched with oxygen mixed into the stream were used as the raw materials. According to the chromatographic analysis, the amount of oxygen in the air is 19.8%, nitrogen - 80.2% by volume.

The catalytic activity of the synthesized samples was studied in a flow-type device at a relative volume flow rate of 1000 h-1, pressure of 1 atm, temperature of 600-900ºC, catalyst volume of 25 - 75 cm3, and granule size of 0.25 mm - 0.5 mm on a solid catalyst bed.

The experiments were carried out at the upper explosion limit (gas-air mixture by volume of 15%). In this regard, methane was first supplied from the cylinder to the mixing section. Air was additionally passed through a dryer before mixing. Gas flow rates were recorded using differential pressure gauges. The reactor has a quartz tube with a thermocouple pocket in the center. Reactor diameter - 8 mm, length - 650 mm. The required temperature is created using two VNO-2 heaters. The temperature was controlled and recorded using two parallel PID controllers OVEN-TRM-10. Before the test, an "isothermal zone" was established. The reactor was filled with inert ceramic balls and heated to operating temperature. The temperature is then measured along the layer height. A working area with a temperature gradient of no more than 10ºC was selected for the process.

The products are condensed in an air cooler, then the product mixture enters a desiccant (calcium chloride) to remove water vapor, and then a sampler.

Experimental studies were carried out in a flow-type laboratory setup to study the process of competitive adsorption of methane oxycondensation process products (see Fig.1).



**FIGURE 1.** Laboratory setup for adsorption studies.

The gas mixture first passes through an absorber containing a hydroxide solution to remove carbon dioxide and a dryer to remove water. The adsorber is a quartz tube 400 mm long and 3 mm in diameter, with a perforated grid on the bottom of which the adsorbent lies and a pocket for a thermocouple. The temperature in the adsorber is maintained by an electrically heated oven and regulated by the TRM-201 device.

During the experiment, a mixture consisting mainly of C2H4, C2H6, H2 and CH4 was passed through an adsorber filled with 10 cm3 of zeolite at a constant linear velocity. By controlling the ethylene concentration in the inlet gas, the adsorption cycle was carried out until the zeolite was completely saturated. In the desorption cycle, the adsorbent was removed from the zeolite by increasing the temperature in the adsorber to 350ºC and spraying the bed with a gas stream. In laboratory tests, atmospheric air was used as the desorbent.

Catalyst samples were synthesized by preparation of precursors based on different manganese salts. Calculated amounts of manganese (II) nitrate, manganese (II) acetate, sodium carbonate (Na2CO3), acetic acid (CH3COOH), nitric acid (HNO3), and distilled water were mixed in precise order. The resulting solution was added to the required amount of silica gel and continuously mixed until a homogeneous mass was formed. Subsequently, the resulting mass was slowly evaporated and completely freed from moisture by thermal drying at 120°C for 3 hours.

After the drying process, the catalyst samples were calcined in air at 900 °C for 6 hours.

The prepared catalysts are intended for oxidative condensation of methane, the main component of natural gas, in the presence of oxygen, and are highly catalytically active, highly selective, and highly productive. The content of Na⁺ ions in the catalyst was 4% by weight, and the proportion of manganese compounds was 10%.

**RESULTS AND DISCUSSION**

To achieve high efficiency in the oxidative condensation of methane, the main component of natural gas, in the presence of oxygen from air, the correct selection of catalyst composition is crucial. To this end, we investigated the catalytic activity of several oxide compounds, specifically MnO2, PbO, and SnO2, in combination with a water-resistant silica gel support. In this study, the main focus was on the ability of oxides to form active sites on the carrier surface, as well as their ability to convert methane molecules into target products such as ethane and ethylene through activation and partial oxidation.

The experimental results quantified the conversion rates of methane to ethane and ethylene, as well as the selectivity exhibited by each catalyst tested. The data obtained differed significantly for different oxide systems, confirming that the type of oxide and its interaction with the support have a significant impact on catalytic efficiency.

The experimental data obtained for the catalysts with high catalytic activity, selectivity, and efficiency, recommended for the oxidative condensation of methane, are presented in Table 1 in a comparative form. This table shows the methane conversion rate, ethane and ethylene yields, and overall selectivity values for different catalyst compositions.

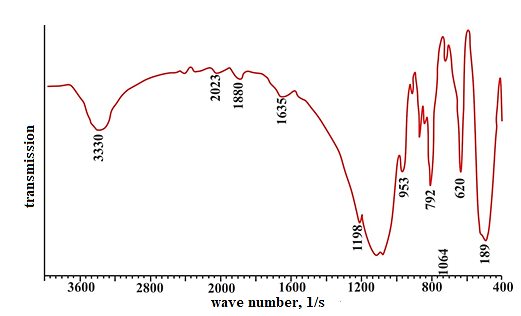
According to the results of the study, a significant increase in selectivity for C₂ hydrocarbons was observed at a temperature of 750°C in the (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ catalyst sample (see Table 1). This is explained by the decrease in the oxidation capacity of the manganese oxide catalytic system in deep oxidation reactions as a result of the interaction of the Mn2O3 phase with the HSZ carrier. That is, this compatibility with the carrier contributes to the production of ethane and ethylene with high selectivity, since the formation of undesirable products such as CO and CO2 as a result of excessive oxidation is reduced.

**TABLE 1.** Temperature dependence of methane conversion rate and selectivity values for C2 hydrocarbons.

|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | **Process temperature, 0С** | **Methane conversion rate, %** | **Selectivity for C2 hydrocarbons** |
| **(Mn2O3)x∙(Na2MoO4)у∙(ZrO2)z/SiO2** | 650 | 32,5 | 36,1 |
| 700 | 43,6 | 41,0 |
| 750 | 50,8 | 79,4 |
| 800 | 49,5 | 68,2 |
| **(Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/ HSZ** | 650 | 38,5 | 41.6 |
| 700 | 47,2 | 53,2 |
| 750 | 52,6 | 81,4 |
| 800 | 49,8 | 72.6 |
| **(Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/Al2O3** | 650 | 25.9 | 24.6 |
| 700 | 37.3 | 36.0 |
| 750 | 48.2 | 67.4 |
| 800 | 39.6 | 59.1 |

Compared with high silica zeolite (HSZ), Al2O3, and SiO2-based analogues, the HSZ-based catalyst exhibited the highest C2 selectivity values at 750°C. This confirms that the nature of the carrier and the interaction of the active phases are one of the important factors that determine the selectivity of the target products during the oxidative condensation of methane.

IR spectroscopic studies (see Fig. 2) showed the presence of absorption bands characteristic of silica gel: 469, 620, 810 and 1110 cm-1, of which 620 and 1110 cm-1 are characteristic of Si-O vibrations in . There are atomic vibrations in the tetrahedron and Si-O-Si: bending at 507 cm-1 and stretching at 954 cm-1, Mn-O - 857 cm-1 and weak stretching vibrations of atoms in the tetrahedron: 901 cm-1. At least two types of H2O molecules are retained on the MnOx-SiO2 surface, as confirmed by the frequency at 1635 cm-1, which corresponds to the bending vibrations of atoms in H2O and is strongly polarized in the Si4+ and Mn4+ regions. 3317 and 3447 cm-1 are cations involved in strong hydrogen bonding, corresponding to widespread diffuse absorption bands.



**FIGURE 2.** IR spectrum of (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ sample

It is known that alkali metal additives have a wide effect on catalysts with high catalytic activity, selectivity and productivity, selected for the oxidative condensation of methane, which is the main component of natural gas, in various processes, including the partial oxidation of organic substances. A number of factors influence the activity of these catalytic systems, the main of which is the neutralization of the carrier's acid centers.

**TABLE 2.** Dependence of contact time on methane conversion and selectivity to ethylene in the oxidative condensation of methane (catalyst (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Temperature, 0С** | **Time of contact, с** | **Conversion of methane to ethane and ethylene ,%** | | **Ethylene selectivity,%** | **Selectivity for C2 hydrocarbons** |
| 650 | 3,5 | 15,8 | 18,2 | | 24,6 |
| 700 | 28,5 | 29,8 | | 45,0 |
| 750 | 31,0 | 31,1 | | 54,4 |
| 800 | 24,3 | 23,1 | | 34,8 |
| 850 | 28,0 | 20,8 | | 41,8 |
| 650 | 2,5 | 28,7 | 37,0 | | 50,1 |
| 700 | 38,9 | 49,2 | | 66,4 |
| 750 | 41,6 | 51,5 | | 77,8 |
| 800 | 37,2 | 42,0 | | 63,5 |
| 850 | 27,5 | 38,0 | | 58,9 |
| 650 | 1,2 | 38,4 | 42,5 | | 66,8 |
| 700 | 46,3 | 56,8 | | 76,2 |
| 750 | 52,6 | 62,4 | | 81,4 |
| 800 | 49,2 | 51,2 | | 78,7 |
| 850 | 41,6 | 41,7 | | 64,7 |

Studies on the concentration of Na⁺ ions have shown that the highest efficiency in the oxidative condensation of methane, the main component of natural gas, in the presence of air oxygen is achieved with a catalyst containing (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ. This catalyst is characterized by high catalytic activity, high selectivity for C2 hydrocarbons (ethane and ethylene), and stable productivity.

Physico-chemical characteristics of prepared catalyst samples are presented in Table 3. The table shows the total volume (VΣ), specific surface area (Ssol), and density (D). It can be seen from the data that the specific surface area (0.24 m2/g) and total volume (0.443 ml/g) of the catalyst with the YuKTs-based carrier is higher than that of the HSZ-based counterpart, which means that it has a better distribution of active centers and more open surface for reaction. At the same time, the density of the HSZ-based catalyst is high (0.99 kg/m3), which is explained by differences in its structure and porosity.

The results also showed that increasing the contact time in the reaction increases the overall conversion of methane to ethane and ethylene, but the selectivity for C2 hydrocarbons decreases. This is explained by the fact that as the contact time increases, the target products are converted into non-valuable products such as CO and CO2 through deep oxidation.

**TABLE 3.** Properties of selected catalysts for oxidative condensation of methane

|  |  |  |
| --- | --- | --- |
| **Catalyst** | **(Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/ SiО2** | **(Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ** |
| **VΣml/g** | 0,427 | 0,443 |
| **Sspe, m2/g** | 0,07 | 0,24 |
| **D, kg/m3** | 0,99 | 0,7 |

**Table 4 and 5 presents the experimental results obtained for testing the** (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ **catalyst. The table provides comparative values of temperature, contact time, methane conversion, and selectivity for C2 hydrocarbons, from which it is possible to determine the optimal operating modes of the catalyst.**

**TABLE 4.** Results of testing the catalyst composed of (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/SiО2

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Temperature, oC** | **Methane consumption, ml /s** | **O2 flow rate ml/s** | **Conversion of methane, the main component of natural gas, to ethane and ethylene,%** | **Ethylene selectivity,%** | **Selective exposure to ethane** | **Selectivity on the C2 hydrocarbon** | **yield** |
| 680 | 6,08 | 2,016 | 26,9 | 28,3 | 6,3 | 34,6 | 9,3 |
| 707 | 6,08 | 2,016 | 35,3 | 24,2 | 2,4 | 26,6 | 9,1 |
| 750 | 6,08 | 2,016 | 42,3 | 20,7 | 2,4 | 23,1 | 7,7 |
| 800 | 6,08 | 2,016 | 37,8 | 17,7 | 0,7 | 18,4 | 6,9 |
| 692 | 6,63 | 2,68 | 45,9 | 21,7 | 2,0 | 23,7 | 10,9 |
| 700 | 6,63 | 2,68 | 37,1 | 25,0 | 2,7 | 27,7 | 10,3 |
| 750 | 6,63 | 2,68 | 43,2 | 15,8 | 0,7 | 16,5 | 7,1 |
| 800 | 6,63 | 2,68 | 44,9 | 10,3 | 1,3 | 11,6 | 5,2 |
| 680 | 8,96 | 4,48 | 23,1 | 24,7 | 9,9 | 34,6 | 8,0 |
| 700 | 8,96 | 4,48 | 22,3 | 24,4 | 9,7 | 34,1 | 7,6 |
| 750 | 8,96 | 4,48 | 24,4 | 21,7 | 10,9 | 32,6 | 8,0 |
| 800 | 8,96 | 4,48 | 26,0 | 20,0 | 10,0 | 30,0 | 7,8 |
| 680 | 7,84 | 5,15 | 50,8 | 13,8 | 4,9 | 18,7 | 9,5 |
| 700 | 7,84 | 5,15 | 54,2 | 13,3 | 4,7 | 18,0 | 9,8 |
| 750 | 7,84 | 5,15 | 64,4 | 10,3 | 2,1 | 12,4 | 8,0 |
| 800 | 7,84 | 5,15 | 75,3 | 7,9 | 1,4 | 9,3 | 7,0 |

**TABLE 5.** (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ Results of testing of a catalyst with high catalytic activity, selectivity and productivity, selected for the oxidative condensation of methane, the main component of natural gas

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Temperature, 0C** | **Methane consumption, ml/s** | **O2 flow rate ml/s** | **Conversion of methane to ethane and ethylene, %** | **Selective sensitivity to ethylene,** | **Selective exposure to ethane** | **Selectivity on the C2 hydrocarbon** | **yield** |
| 680 | 6,08 | 2,016 | 72,0 | 44,6 | 17,3 | 51,9 | 11,4 |
| 707 | 6,08 | 2,016 | 70,1 | 45,9 | 14,5 | 50,4 | 12,1 |
| 750 | 6,08 | 2,016 | 68,7 | 46,4 | 11,4 | 47,8 | 13,2 |
| 800 | 6,08 | 2,016 | 63,9 | 42,4 | 8,1 | 40,5 | 13,7 |
| 692 | 6,63 | 2,68 | 56,5 | 40,3 | 7,2 | 37,5 | 13,7 |
| 700 | 6,63 | 2,68 | 48,6 | 57,5 | 14,0 | 41,5 | 13,9 |
| 750 | 6,63 | 2,68 | 54,4 | 61,8 | 17,1 | 81,2 | 14,9 |
| 800 | 6,63 | 2,68 | 41,3 | 56,5 | 16,4 | 73,9 | 17,4 |
| 680 | 8,96 | 4,48 | 43,7 | 40,1 | 7,6 | 65,5 | 16,2 |
| 700 | 8,96 | 4,48 | 42,1 | 44,7 | 7,9 | 50,2 | 16,3 |
| 750 | 8,96 | 4,48 | 45,2 | 42,1 | 9,8 | 64,7 | 14,4 |
| 800 | 8,96 | 4,48 | 37,6 | 44,7 | 8,5 | 60,0 | 10,6 |
| 680 | 7,84 | 5,15 | 22,5 | 43,0 | 8,2 | 53,9 | 12,1 |
| 700 | 7,84 | 5,15 | 38,5 | 40,1 | 8,9 | 35,3 | 13,6 |
| 750 | 7,84 | 5,15 | 41,4 | 47,5 | 9,4 | 49,2 | 15,4 |
| 800 | 7,84 | 5,15 | 32,8 | 44,8 | 8,06 | 44,9 | 14,7 |
| 680 | 6,08 | 2,016 | 29,6 | 49,8 | 7,2 | 54,5 | 16,1 |
| 707 | 6,08 | 2,016 | 33,8 | 42,6 | 8,2 | 43,6 | 14,7 |
| 750 | 6,08 | 2,016 | 33,3 | 38,6 | 9,8 | 37,9 | 12,6 |

**CONCLUSION**

This study investigated the catalytic conditions for the production of ethylene and ethane by oxidative condensation of methane, the main component of natural gas. The experimental reactions were carried out using a flow-type reactor at temperatures ranging from 600 to 900 °C and a pressure of 1 atmosphere. The catalyst granules were sized from 0.25 to 0.5 millimeters, and the relative space velocity was maintained at 1000 per hour. The experiments used a 15 percent gas-air mixture in accordance with safety protocols.

Factors affecting the activity of catalysts—the nature of the carrier, temperature, contact time, and concentration of Na⁺ ions—were studied separately. The (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ catalyst was characterized by high conversion and selectivity. As temperature increases, the conversion of methane to ethane and ethylene increases, but the selectivity for C2 hydrocarbons decreases at a certain temperature. The optimal temperature was found to be around 750–800°C.

According to the results of IR spectroscopic analyses, the vibrational frequencies of the Si–O, Mn–O, and H–O bonds on the catalyst surface were determined, which confirmed the metal–carrier interaction and adsorption properties. The conditions for successful separation and desorption of C2 hydrocarbons in zeolite adsorbers were determined.

Catalysts synthesized on different supports (SiO2, Al2O3, high-silica zeolite) were comparatively analyzed. The catalyst based on high-silica zeolite showed maximum selectivity and efficiency. This is explained by the limitation of the oxidation capacity of manganese oxide due to its interaction with silica gel.

In general, the catalyst composed of (Mn2O3)x∙(Na2MoO4)y∙(ZrO2)z/HSZ has been proven to be of practical importance as an energy-efficient and environmentally friendly method for increasing the value of natural gas and processing it. Based on the obtained results, this technology can be considered as one of the promising directions for obtaining ethylene directly from methane in industry.

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