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Д.В.Сокольский атындағы «Жанармай,  
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# Х А Б А Р Л А Р Ы

## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
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## NEWS

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**METHANE CONVERSION OVER Mo/Al<sub>2</sub>O<sub>3</sub> – CATALYSTS MODIFIED WITH ADDITIVES OF ZEOLITE AND PHOSPHOROUS**

**Abstract.** Mo-containing catalysts supported on a matrix consisting of alumina modified with additives of both zeolite – HZSM and phosphorus were synthesized. The molybdenum content was varied within a range of 1-5 mas.%. The physicochemical properties of the catalysts were studied by BET, XRD, electron microscopy, and microdiffraction analysis. The catalytic properties of the synthesized catalysts were tested in the processes of dry and combined steam-dry conversion of methane. It was shown that the synthesized catalysts are the nanosystems with particle sizes are 3-50 nm depending on the amount of molybdenum and the processing methods of the catalysts. The activity of the catalysts grows with increasing of both molybdenum content and temperature. The main product of methane conversion is synthesis gas. The H<sub>2</sub>/CO ratio increases at adding steam to an initial feed. In dry reforming of methane the reaction products also contain C<sub>2</sub>, C<sub>6</sub> hydrocarbons and alcohols.

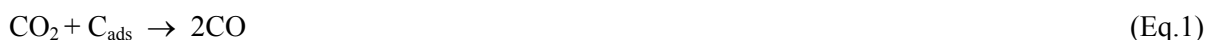
**Key words:** Dry and Combined Dry-Steam Conversion of Methane, Syngas, Molybdenum, Zeolite, Phosphorus.

**1. INTRODUCTION**

In recent years, the processing of gaseous hydrocarbons into value-added products has attracted attention. Conversion of methane, the primary constituent of natural gas, associated petroleum gas, biogas is considered to be the promising one. Biogas is considered as a renewable source of energy [1].

One of the ways of conversion methane-containing feedstock to chemicals is production of synthesis gas [2]. There are three reforming reactions that allow converting methane into syngas with different H<sub>2</sub>/CO ratio: partial oxidation, steam reforming, and dry reforming [3]. The last one has gained a lot of attention due to possibility to reduce the emissions of two main greenhouse gases like carbon dioxide and methane [4]. The ratio of H<sub>2</sub>/CO produced in the dry reforming of methane is ~ 1 which preferable as a feed for production long chain hydrocarbons and oxygenates [5, 6].

The main challenge is that the reaction is highly endothermic and high temperatures are required to reach considerable extent of conversion as well as surpass side reactions [7, 8]. Lack of stable catalysts against quick deactivation because of coking and active sites sintering is another disadvantage [2,9]. To reduce the undesirable carbon deposition process, it is necessary to create an active catalyst and technology capable of involving the surface C<sub>ads</sub> formed as a result of the destructive decomposition of methane into interaction with CO<sub>2</sub> (Eq.1). Surface adsorbed carbon is the product of the complete dehydrogenation of a methane molecule during its carbon dioxide conversion at the metal-containing active center of the catalyst.



Therefore more efforts are being expended in the development of new catalysts that will represent activity, resistance to coking, as well as, long-term stability. Non-noble metals like Ni, Co, Fe and noble metals including Pt, Rh, Ir, Pd and etc. have been studied as a catalyst in the dry reforming of methane [10-13]. Non-noble-based catalysts are preferable over noble metals because of the availability and low cost. Noble metals are usually applied as a promoter in polymetallic catalysts due to their high activity and greater resistance to coke formation compared to non-noble metals [14]. It allows overcoming the

deactivation of non-noble catalysts caused by excessive coke deposition, while simultaneously reducing total cost. Other benefits of this approach are it increases the dispersion of the metal, decreases the size of the metal particle and thus retain a good catalytic activity and stability.

Supported transition metals (or their carbides) are another type of catalysts that have attracted attention due to their comparable activity and stability to noble metals [8,15-16]. The performance of a catalyst does not depend not only on active metal and promoter, but also on the support. Main role of supports is in provision of certain textural and physicochemical properties [17]. These properties give possibility to a catalyst to stay well-dispersed and resistant to carbon deposition. Single-metal support such as  $\gamma$ -alumina performs very well in the reforming of methane, but it is apparent that mixed and/or structured supports have properties that make them attractive to use in methane reforming [11]. Zeolites with a high Si/Al ratio are considered to give better conversions, which are more basic. Their good performance is due to the confinement of active metal particles inside their pores, providing a higher resistance to sintering, as well as their basic character that decreases carbon deposition [18].

In this work, the new Mo-containing catalysts supported on alumina modified with additives of zeolite (HZSM-5) and phosphorus were synthesized and tested in dry and combined steam-dry reforming of methane.

## 2. EXPERIMENTAL

Catalysts were prepared by mixing  $\text{Al}(\text{OH})_3$  with HZSM-5 zeolite followed by drying and forming of the granules and their calcination. The ratio  $\text{Al}_2\text{O}_3$ :HZSM=7:3. The prepared by such a way matrix was impregnated by molybdenum salt and phosphoric acid. The molybdenum content varied from 1 to 5 mas.% by weight of the catalyst, the phosphorus content – 1.0 mas. %.

The model feed corresponding to biogas composed of  $\text{CH}_4$  – 53.5 vol. %,  $\text{CO}_2$  – 46.5 vol. % was used for dry reforming of methane (DRM). For combined steam-dry conversion of methane or so-called bireforming of methane (BRM), 20 vol.% of steam was added to an initial feed. The ratio (vol.) of the components in the feedstock was:  $\text{CH}_4$ : $\text{CO}_2$ : $\text{H}_2\text{O}$ =1.15:1.0:0.2. The process was carried out in a laboratory flow quartz reactor operated under atmospheric pressure at varying temperature within 500-1000°C and the gas hourly space velocity (GHSV) was varied from 500 to 1000  $\text{h}^{-1}$ .

The physicochemical properties of the catalysts were studied by XRD, BET, TEM, and microdiffraction analysis.

The initial and final reaction products were analyzed by on-line GC. The conversion degrees of carbon dioxide ( $X_{\text{CO}_2}$ ) and the methane ( $X_{\text{CH}_4}$ ) were calculated according to formulas (1, 2) respectively. Thus, the activity of catalysts was compared.

$$X_{\text{CO}_2} = ([\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}) \cdot 100\% / [\text{CO}_2]_{\text{in}} \quad (1)$$

$$X_{\text{CH}_4} = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) \cdot 100\% / [\text{CH}_4]_{\text{in}} \quad (2)$$

where  $[\text{CH}_4]_{\text{in}}$  and  $[\text{CO}_2]_{\text{in}}$  – mole fraction of  $\text{CH}_4$  and  $\text{CO}_2$  in inlet stream,  $[\text{CH}_4]_{\text{out}}$  and  $[\text{CO}_2]_{\text{out}}$  – mole fraction of  $\text{CH}_4$  and  $\text{CO}_2$  in outlet stream.

Conversion of water was not calculated.

Yields of reaction products: hydrogen, carbon oxide and hydrocarbons ( $Y_{\text{H}_2}$ ,  $Y_{\text{CO}}$  and  $Y_{\text{C}_n}$  respectively) expressed as its amount ( $\mu\text{mol}$ ) formed by gram of the catalyst per second ( $\mu\text{mol}/(\text{g}\cdot\text{s})$ ).

## 3. RESULTS AND DISCUSSION

### 3.1 Catalyst characterization

The specific surface area (BET) and pore volume of both fresh and spent samples of the Mo catalysts in the dry conversion of methane were determined. The fresh catalyst samples with varied Mo content have the same characteristics. The difference was observed between the fresh and spent samples of 2% Mo/ $\text{Al}_2\text{O}_3$ -HZSM-P, which was long-term tested (for 30 hours) in BRM. Specific surface area was decreased from 307.1 to 201.7  $\text{m}^2/\text{g}$ , while pore volume was not significantly changed: 296.8 and 290.8  $\text{ml}/\text{g}$  for fresh and spent samples respectively (Table 1).

Table 1 – The specific surface of 2%Mo/Al<sub>2</sub>O<sub>3</sub>-HZSM-P catalysts (BET)

| S, m <sup>2</sup> /g |              | V, ml/g |              |
|----------------------|--------------|---------|--------------|
| fresh                | spent (30 h) | fresh   | spent (30 h) |
| 307.1                | 201.7        | 296.8   | 290.8        |

The XRD method did not show the presence of any structures except alumina in the catalysts due to possibly high dispersed state of the catalysts and therefore they are X-ray amorphous. Other reason may be a low metal content, the determination of which is outside the sensitivity range of the equipment.

Studies of the 2%Mo/Al<sub>2</sub>O<sub>3</sub>-HZSM-P catalyst (fresh) by TEM showed an accumulation of dense particles of a prismatic shape and translucent laminated particles with sizes of 30-70 nm (Fig. 1). The microdiffraction pattern is represented by a small number of rings composed of reflections assigned to a mixture of phases: Mo<sub>3</sub>Si (JCPDS, 4-814) and AlMo<sub>3</sub> (JCPDS 11-18).

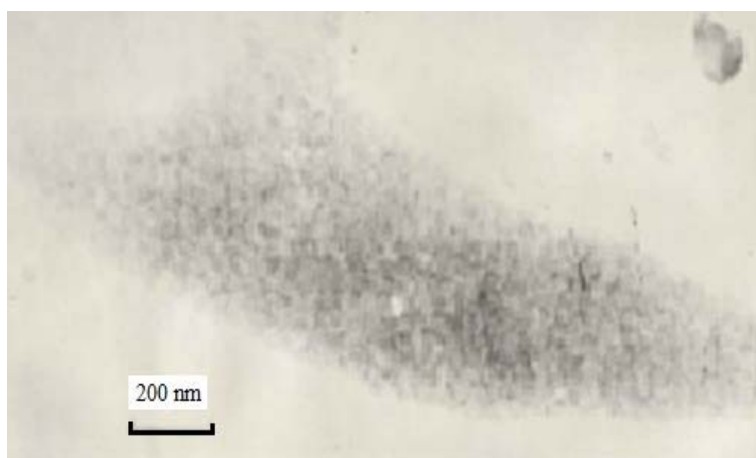


Figure 1 – TEM image of the fresh sample 2%Mo /Al<sub>2</sub>O<sub>3</sub>-HZSM-1%P catalyst

Also, the particles with a size of 30–50 nm were observed. Their microdiffraction pattern can be attributed to Mo<sub>3</sub>Si (JCPDS, 4-814). The small particles with a size of 8-10 nm give the microdiffraction pattern, which corresponds to SiP structure (JCPDS, 27-608). The presence of Mo<sub>3</sub>Si and SiP structures in the catalyst indicates the entry of Mo and phosphorus into the zeolite framework.

A large aggregate composed of translucent lamellar particles of predominantly 10-30 nm correspond to AlPO<sub>4</sub> (JCPDS, 31-28). At low magnification, the translucent lamellar particles were detected. The microdiffraction pattern is represented by reflections located in rings and separate reflexes and can be assigned to a mixture of phases: AlPO<sub>4</sub> in the modification (JCPDS, 20-45) and MoOPO<sub>4</sub> (JCPDS, 18-942). The presence of two modifications of AlPO<sub>4</sub> may be explained by the interaction of phosphorus with aluminum in zeolite framework and aluminum in Al<sub>2</sub>O<sub>3</sub>.

### 3.2 Dry reforming of methane on Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst

The effect of temperature on the performance of the 1%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst in dry reforming of methane (DRM) has been studied under conditions: CH<sub>4</sub>/CO<sub>2</sub>=1.15, P=0.1MPa, GHSV=1000h<sup>-1</sup> and varying temperature within 775-1000°C. The degrees of methane and carbon dioxide conversion grow from 1.7 to 31.1 and 21.3 to 65.2% respectively with an increase in temperature from 775 to 1000°C.

In the entire temperature range studied, the main product of DRM over the 1%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst is synthesis gas. Traces of C<sub>2</sub>, C<sub>6</sub> hydrocarbons and traces of oxygenates are also formed. Increasing temperature leads to growing the hydrogen content in the synthesis gas formed. Thus, an increase in temperature from 775 to 1000°C causes an increase in the H<sub>2</sub>/CO ratio from 0.5 to 1.1. At high temperatures of 900-1000°C traces of oxygenates (C<sub>1</sub>-C<sub>2</sub> alcohols) are formed. In the temperature range of

800-900°C, traces of C<sub>2</sub> and C<sub>6</sub> hydrocarbons are detected. At 1000°C, ethylene is formed in an amount of 0.2% (Table 2). The formation of these products occurs due to the interaction of alkyl and methylene surface-adsorbed fragments of incomplete methane destruction. The ability of Mo/HZSM catalysts to convert methane to benzene is well-known [19].

Table 2 – The effect of the process temperature on DRM over the 1%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> at CH<sub>4</sub>:CO<sub>2</sub>=1.15:1, GHSV=1000h<sup>-1</sup>, P=0.1MPa

| t, °C | Conversion, %    |                  | H <sub>2</sub> /CO | Yield of products                    |                   |
|-------|------------------|------------------|--------------------|--------------------------------------|-------------------|
|       | X <sub>CH4</sub> | X <sub>CO2</sub> |                    | hydrocarbons                         | oxygenates        |
| 800   | 8.2              | 21.5             | 0.5                | C <sub>6</sub> (traces)              | -                 |
| 900   | 19.6             | 42.1             | 0.8                | C <sub>2</sub> (traces)              | alcohols (traces) |
| 1000  | 31.1             | 65.2             | 1.1                | C <sub>2</sub> H <sub>4</sub> - 0.2% | alcohols (traces) |

It is known that in the process of methane dehydrocyclization over the Mo/HZSM catalyst along with the formation of benzene, significant carbonization of the catalytic surface occurs. Microdiffraction and TEM data on Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> studied confirm the formation of a nanosystem containing the various surface structures due to interaction molybdenum with zeolite and alumina to form Mo<sub>3</sub>Si and Al<sub>2</sub>Mo<sub>3</sub>. Modification of the Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst with phosphorus leads to formation of MoOPO<sub>4</sub> structure. Phosphorus also can be included into the zeolite framework as SiP and AlPO<sub>4</sub>. Interaction between phosphorus and alumina with formation of AlPO<sub>4</sub> was previously shown [20]. The multicomponent chemical composition of the catalytic surface due to modification by phosphorus leads to the suppression of the formation of benzene and C<sub>2</sub>- hydrocarbons. The formation of synthesis gas becomes the main direction of carbon dioxide conversion of methane over the Mo-P-HZSM composed catalyst.

The catalytic processing of methane and other hydrocarbons is accompanied by the appearance of carbon deposits on the active catalyst sites. The effect of C<sub>ads</sub> on the catalyst activity will depend on the nature of metal. Mo is able to form carbides with C<sub>ads</sub>.

With an increase in the temperature of DRM from 800°C to 1000°C the reaction products mainly contain synthesis gas, the H<sub>2</sub>/CO ratio increases from 0.5 to 1.2, which is associated with prevailing destructive decomposition of methane on Mo containing centers. In this case, the C<sub>ads</sub> formed can interact with CO<sub>2</sub>, but at a low concentration of CO<sub>2</sub> the C<sub>ads</sub> can be introduced into the molybdenum structure with the formation of carbide – Mo<sub>2</sub>C.

Comparative analysis of data [19,21-22] and results of this study allows to conclude that the formation and destruction of molybdenum carbide depend on the carbon dioxide content in the reaction zone. At a low concentration of CO<sub>2</sub> in the feedstock C<sub>ads</sub> formed can interact with molybdenum to form carbides at high temperatures. At high CO<sub>2</sub> concentrations in the feed, carbide is destroyed as a result of the reaction (Eq.2) [21-22]. Molybdenum carbide is an active catalyst for dry reforming of methane.



### 3.3 Bireforming of methane on Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalysts

To enrich the synthesis gas with hydrogen, the steam additives (20 vol.%) were introduced into the feed CH<sub>4</sub>-CO<sub>2</sub>. The combined dry-steam reforming of methane or bireforming of methane (BRM) was carried out over the 1%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst under P=0.1MPa, GHSV=1000h<sup>-1</sup>, CH<sub>4</sub>:CO<sub>2</sub>:H<sub>2</sub>O=1.15:1.0:0.2 and varying temperature within a range of 500-1000°C.

At a temperature of 1000°C, the degree of conversion of methane and carbon dioxide reaches 43.7 and 78.2% respectively (Fig.2). Conversion of carbon dioxide is higher because its content in initial feed is less. The main product of BRM is synthesis gas. H<sub>2</sub>/CO ratio is increased from 0.6 to 1.2 at growing temperature from 800 to 1000°C. The addition of steam into the reaction mixture inhibits the formation of hydrocarbons. C<sub>2</sub> and C<sub>6</sub> hydrocarbons and oxygenates presented in small amounts at relatively low temperature – 780°C and completely disappeared at higher temperatures (Table 3).



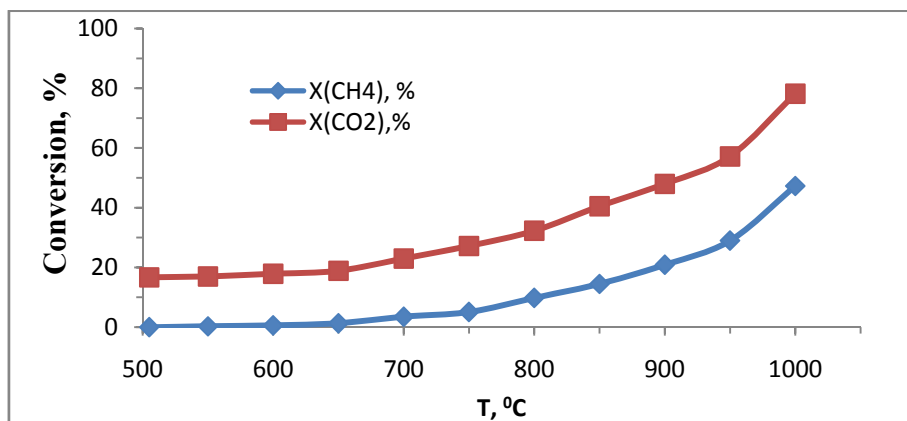


Figure 2 – The effect of temperature on BRM over the 1% Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst at CH<sub>4</sub>:CO<sub>2</sub>:H<sub>2</sub>O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h<sup>-1</sup>

Table 3 – Effect of temperature on the products composition in BRM over the 1%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst at CH<sub>4</sub>:CO<sub>2</sub>:H<sub>2</sub>O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h<sup>-1</sup>

| t, °C | Conversion, %               |                             | H <sub>2</sub> /CO | Product yield   |            |
|-------|-----------------------------|-----------------------------|--------------------|---|------------|
|       | X <sub>CH<sub>4</sub></sub> | X <sub>CO<sub>2</sub></sub> |                    | Hydrocarbons  | Oxygenates |
| 780   | 9.1                         | 29.0                        | 0.6                | C <sub>2</sub> H <sub>4</sub> , C <sub>6</sub> (traces) | traces     |
| 800   | 9.8                         | 32.3                        | 0.6                | -   | traces     |
| 900   | 20.9                        | 48.0                        | 0.8                | -   | traces     |
| 1000  | 47.3                        | 78.2                        | 1.2                | -   | traces     |

The analysis of Tables 2 and 3 shows that the participation of steam in methane conversion leads to increase in conversion both of methane and carbon dioxide as well as to enrich synthesis gas with hydrogen. Consumption of carbon dioxide is higher than methane i.e. CO<sub>2</sub> may actively reacts with C<sub>ads</sub> with formation of CO at the Mo-containing centers.

Mainly, the optimal amount of the active component of the catalyst is experimentally determined. In this work, the Mo content ranged from 1 to 5 mas. % weight. Figure 3 shows the effect of temperature on the conversion of CH<sub>4</sub> and CO<sub>2</sub> in BRM over the 2%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst. The high activity of the catalyst in BRM is observed at a temperature region of 800-1000°C: methane conversion was 72.4 and carbon dioxide – 86% at 960°C. The main reaction product over the 2%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst is synthesis gas, the H<sub>2</sub>/CO ratio is 1.3.

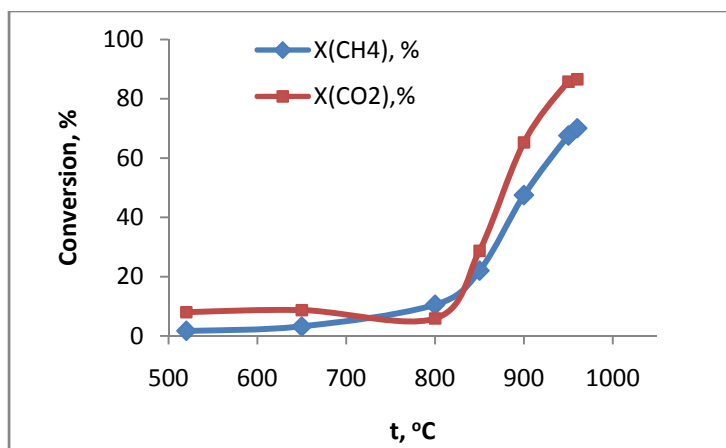


Figure 3 – The effect of temperature on BRM over the 2% Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst at CH<sub>4</sub>:CO<sub>2</sub>:H<sub>2</sub>O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h<sup>-1</sup>

At using higher content of Mo – 5 mas.% under the same conditions ( $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}=1.15:1:0.2$ ,  $P=0.1$  MPa,  $\text{GHSV}=1000\text{h}^{-1}$ ) an increase in activity of the 5%Mo/HZSM-P- $\text{Al}_2\text{O}_3$  catalyst was observed in BRM. Methane conversion became higher than carbon dioxide (Fig. 4):  $X_{\text{CH}_4}=82.0\%$ , while  $X_{\text{CO}_2}=65.8\%$  at  $960^\circ\text{C}$ .

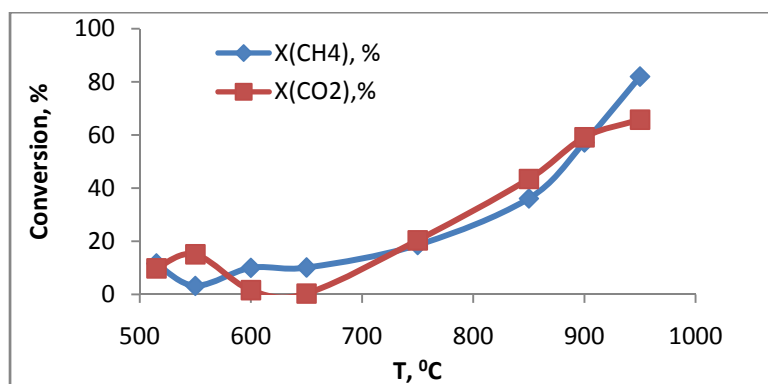


Figure 4 – The effect of temperature on BRM over the 5% Mo/HZSM-P- $\text{Al}_2\text{O}_3$  catalyst at  $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}=1.15:1:0.2$ ,  $P=0.1$  MPa,  $\text{GHSV}=1000\text{h}^{-1}$

Thus, systematic studies of Mo/HZSM-P- $\text{Al}_2\text{O}_3$  catalysts with varying molybdenum contents from 1.0 to 5 wt.% allowed us to conclude that the activity is directly dependent on the amount of molybdenum, which is the active phase of the system (Table 4).

Table 4 – Comparative characteristics of Mo/HZSM-P- $\text{Al}_2\text{O}_3$  catalysts in BRM at  $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}=1.15:1:0.2$ ,  $P=0.1$ MPa,  $t=960^\circ\text{C}$ ,  $\text{GHSV}=1000\text{h}^{-1}$

| Mo content, mas. % | Conversion, %     |                   |
|--------------------|-------------------|-------------------|
|                    | $X_{\text{CH}_4}$ | $X_{\text{CO}_2}$ |
| 1                  | 47.3              | 78.2              |
| 2                  | 72.4              | 86.0              |
| 5                  | 82.0              | 65.8              |

The physicochemical properties of the 2%Mo/HZSM-P- $\text{Al}_2\text{O}_3$  catalyst were studied after its long-term operation (30 hours) in BRM by electron microscopy and microdiffraction analysis. In addition to the structures observed in the fresh sample the new species with a size of 10-40 nm (Fig. 5), which can be attributed to a mixture of phases:  $\text{MoO}_2$  (JCPDS, 32-671),  $\eta\text{-MoC}$  (JCPDS, 8-384),  $\alpha\text{-Mo}_2\text{C}$  (JCPDS, 35-787), P (JCPDS, 18-964), SiC (JCPDS, 29-1127),  $\text{Al}_2\text{Mo}_3\text{C}$  (JCPDS 6-7) were detected by microdiffraction analysis.

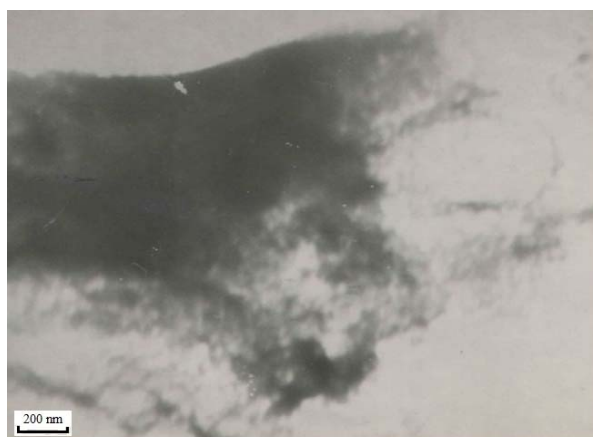


Figure 5 - TEM image of 2%Mo/HZSM-P- $\text{Al}_2\text{O}_3$  spent in BRM for 30 hours

It is more important the appearance of molybdenum carbides: MoC and Mo<sub>2</sub>C. Molybdenum carbides are formed at temperatures above 600-650°C. Under the conditions of BRM molybdenum carbides may be formed due to interaction between atomic carbons formed as a result of methane destruction with Mo which is an active center of the catalyst.

It was shown in [22,23] that molybdenum catalysts coated with Mo carbides exhibit high activity in the carbon dioxide conversion of methane. Molybdenum carbides are highly active in methane conversion that was confirmed in this work by the long-term test of 2%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> in BRM. But over time, the degree of methane conversion decreases as a result of the interaction of carbides with carbon dioxide to form carbon monoxide and non-active molybdenum oxides (Eq.2).

The stability of the 2%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst was tested for long continuous operation (30 hours). The results prove that Mo-containing catalysts are sufficiently thermally stable; no destruction of their structure and particle agglomeration was observed by TEM. Measurement of the surface area of 2%Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst by the BET method showed that some changes occur in the spent sample – S=201.7m<sup>2</sup>/g compared to the initial one –S=307m<sup>2</sup>/g. Elucidation and elimination of the reasons leading to a decrease in the specific surface area of the catalyst after long-term operation will allow the development of methods to increase stability and activity of the Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalyst.

## CONCLUSIONS

Phosphorus modified molybdenum catalysts can be of practical interest in the production of chemical and petrochemical products from any methane-containing feedstock including renewable biogas. The Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> catalysts developed perform the activity and selectivity in syngas production by dry and bireforming of methane. Preliminary stability test demonstrates their stable activity and selectivity for 30 hours of exploitation. Under certain conditions hydrocarbons and alcohols are formed over the catalysts. That allows considering the Mo/HZSM-P-Al<sub>2</sub>O<sub>3</sub> as promising base for manufacturing a cheap stable catalyst for syngas production from methane or biogas by further appropriate modification of the catalyst developed.

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## ФОСФОР ЖӘНЕ ЦЕОЛИТ ҚОСПАСЫМЕН МОДИФИЦИРЛЕНГЕН Mo/Al<sub>2</sub>O<sub>3</sub>- КАТАЛИЗАТОРЛАРДАҒЫ МЕТАННЫҢ ТҮРЛЕНУІ

**Аннотация.** Цеолит (HZSM) және фосфордың қоспаларымен модифицирленген алюминий тотығынан тұратын матрицаға кондырылған Мо-құрамды катализаторлар синтезделген болатын. Молибден мөлшері 1-5 мас.% шамасы аралығында тербеледі. Катализаторлардың физика-химиялық қасиеттері БЭТ, РФА, электронды микроскоп және микродифракциялық анализ әдістерімен зерттелді. Синтезделген катализаторлардың катализдік қасиеттері метанның көмірқышқылды және булы көмірқышқылды түрлену (конверсия) процестерінде тестілеуден өтті. Синтезделген катализаторлар молибденнің мөлшеріне және катализаторларды өңдеу тәсілдеріне байланысты бөлшектер шамасы 3-50 нм-ді құрайтын наножүйеге жататыны көрсетілді. Катализаторлар белсенділігі молибден мөлшері мен температураның ұлғаюына қарай өседі. Метан түрленуінің негізгі өнімі синтез-газ болып табылады. H<sub>2</sub>/CO қатынасы бастапқы газ қоспасына су буын қосу есебінен өседі. Сондай-ақ, метанның сусыз риформингі кезінде реакция өнімдерінде C<sub>2</sub>, C<sub>6</sub> көмірсутектердің және спирттердің азғантай мөлшері құрайды.

**Түйін сөздер:** Метанның Көмірқышқылды және Булы көмірқышқылды Түрленуі (Конверсиясы), Синтез-газ, Молибден, Цеолит, Фосфор.

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### КОНВЕРСИЯ МЕТАНА НА Mo/Al<sub>2</sub>O<sub>3</sub> – КАТАЛИЗАТОРАХ, МОДИФИЦИРОВАННЫХ ДОБАВКАМИ ФОСФОРА И ЦЕОЛИТА

**Аннотация.** Были синтезированы Mo-содержащие катализаторы, нанесенные на матрицу, состоящую из оксида алюминия, модифицированного добавками цеолита – HZSM и фосфора. Содержание молибдена варьировалось в пределах 1-5 мас.%. Физико-химические свойства катализаторов изучались методами БЭТ, РФА, электронной микроскопии и микродифракционного анализа. Каталитические свойства синтезированных катализаторов тестировались в процессах углекислотной и пароуглекислотной конверсии метана. Было показано, что синтезированные катализаторы относятся к наносистемам, размеры частиц которых составляют 3-50 нм в зависимости от количества молибдена и методов обработки катализаторов. Активность катализаторов возрастает с увеличением содержания молибдена и температуры. Основным продуктом конверсии метана является синтез-газ. Соотношение H<sub>2</sub>/CO возрастает при добавлении паров воды в исходную смесь. При сухом риформинге метана в продуктах реакции также содержатся в небольших количествах углеводороды C<sub>2</sub>, C<sub>6</sub> и спирты.

**Ключевые слова:** Углекислотная и Пароуглекислотная Конверсия Метана, Синтез-Газ, Молибден, Цеолит, Фосфор.

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