N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2019.2518-1491.76**
Volume 6, Number 438 (2019), 70 – 78

Y.Y. Nurmakanov, G.D. Zakumbaeva, S.S. Itkulova, and L.V. Komashko

[1]D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan
e-mail: s.itkulova@ifce.kz

METHANE CONVERSION OVER Mo/Al_2O_3 – 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_2/CO ratio increases at adding steam to an initial feed. In dry reforming of methane the reaction products also contain C_2, C_6 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_2/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_2/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_{ads} formed as a result of the destructive decomposition of methane into interaction with CO_2 (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.

$$CO_2 + C_{ads} \rightarrow 2CO \qquad \text{(Eq.1)}$$

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 γ-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 $Al(OH)_3$ with HZSM-5 zeolite followed by drying and forming of the granules and their calcination. The ratio Al_2O_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 CH_4 – 53.5 vol. %, 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: CH_4:CO_2:H_2O=1.15:1.0:0.2. The process was carried out in a laboratory flow quarts 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 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_{CO2}) and the methane (X_{CH4}) were calculated according to formulas (1, 2) respectively. Thus, the activity of catalysts was compared.

$$X_{CO2} = ([CO_2]_{in} - [CO_2]_{out}) \cdot 100\% / [CO_2]_{in} \quad (1)$$

$$X_{CH4} = ([CH_4]_{in} - [CH_4]_{out}) \cdot 100\% / [CH_4]_{in} \quad (2)$$

where $[CH_4]_{in}$ and $[CO_2]_{in}$ – mole fraction of CH_4 and CO_2 in inlet stream, $[CH_4]_{out}$ and $[CO_2]_{out}$ – mole fraction of CH_4 and CO_2 in outlet stream.

Conversion of water was not calculated.

Yields of reaction products: hydrogen, carbon oxide and hydrocarbons (Y_{H2}, Y_{CO} and Y_{Cn} respectively) expressed as its amount (μmol) formed by gram of the catalyst per second (μmol/(g·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/Al_2O_3-HZSM-P, which was long-term tested (for 30 hours) in BRM. Specific surface area was decreased from 307.1 to 201.7 m^2/g, while pore volume was not significantly changed: 296.8 and 290.8 ml/g for fresh and spent samples respectively (Table 1).

Table 1 – The specific surface of 2%Mo/Al_2O_3-HZSM-P catalysts (BET)

S,m^2/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_2O_3-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_3Si (JCPDS, 4-814) and $AlMo_3$ (JCPDS 11-18).

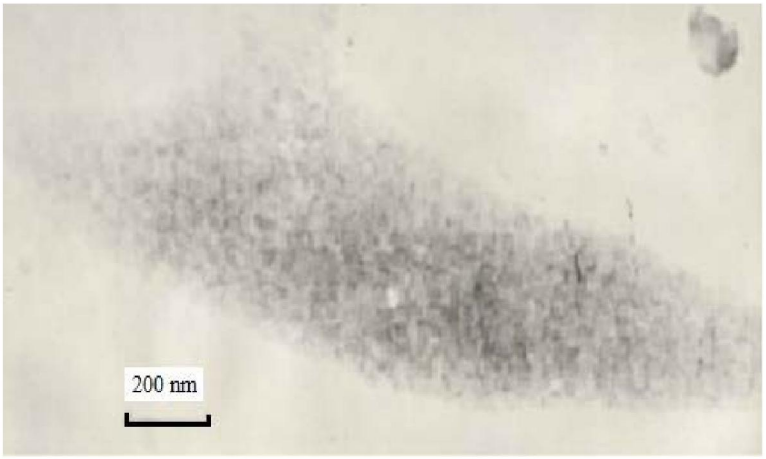

Figure 1 – TEM image of the fresh sample 2%Mo /Al_2O_3-HZSM-1%P catalyst

Also, the particles with a size of 30–50 nm were observed. Their microdiffraction pattern can be attributed to Mo_3Si (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_3Si 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 $AlPO_4$ (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: $AlPO_4$ in the modification (JCPDS, 20-45) and $MoOPO_4$ (JCPDS, 18-942). The presence of two modifications of $AlPO_4$ may be explained by the interaction of phosphorus with aluminum in zeolite framework and aluminum in Al_2O_3.

3.2 Dry reforming of methane on Mo/HZSM-P-Al_2O_3 catalyst

The effect of temperature on the performance of the 1%Mo/HZSM-P-Al_2O_3 catalyst in dry reforming of methane (DRM) has been studied under conditions: CH_4/CO_2=1.15, P=0.1MPa, GHSV=1000h^{-1} 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_2O_3 catalyst is synthesis gas. Traces of C_2, C_6 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_2/CO ratio from 0.5 to 1.1. At high temperatures of 900-1000°C traces of oxygenates (C_1-C_2 alcohols) are formed. In the temperature range of

800-900°C, traces of C_2 and C_6 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_2O_3 at CH_4:CO_2=1.15:1, GHSV=1000h^{-1}, P=0.1MPa

t,°C	Conversion, %		H_2/CO	Yield of products	
	X_{CH4}	X_{CO2}		hydrocarbons	oxygenates
800	8.2	21.5	0.5	C_6 (traces)	-
900	19.6	42.1	0.8	C_2 (traces)	alcohols (traces)
1000	31.1	65.2	1.1	C_2H_4 - 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_2O_3 studied confirm the formation of a nanosystem containing the various surface structures due to interaction molybdenum with zeolite and alumina to form Mo_3Si and Al_2Mo_3. Modification of the Mo/HZSM-P-Al_2O_3 catalyst with phosphorus leads to formation of $MoOPO_4$ structure. Phosphorus also can be included into the zeolite framework as SiP and $AlPO_4$. Interaction between phosphorus and alumina with formation of $AlPO_4$ 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_2- 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_{ads} on the catalyst activity will depend on the nature of metal. Mo is able to form carbides with C_{ads}.

With an increase in the temperature of DRM from 800°C to 1000°C the reaction products mainly contain synthesis gas, the H_2/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_{ads} formed can interact with CO_2, but at a low concentration of CO_2 the C_{ads} can be introduced into the molybdenum structure with the formation of carbide – Mo_2C.

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_2 in the feedstock C_{ads} formed can interact with molybdenum to form carbides at high temperatures. At high CO_2 concentrations in the feed, carbide is destructed as a result of the reaction (Eq.2) [21-22]. Molybdenum carbide is an active catalyst for dry reforming of methane.

$$Mo_2C + CO_2 \rightarrow 2CO + MoO_2 \qquad \text{(Eq.2)}$$

3.3 Bireforming of methane on Mo/HZSM-P-Al_2O_3 catalysts

To enrich the synthesis gas with hydrogen, the steam additives (20 vol.%) were introduced into the feed CH_4-CO_2. The combined dry-steam reforming of methane or bireforming of methane (BRM) was carried out over the 1%Mo/HZSM-P-Al_2O_3 catalyst under P=0.1MPa, GHSV=1000h^{-1}, CH_4:CO_2:H_2O=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_2/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_2 and C_6 hydrocarbons and oxygenates presented in small amounts at relatively low temperature – 780°C and completely disappeared at higher temperatures (Table 3).

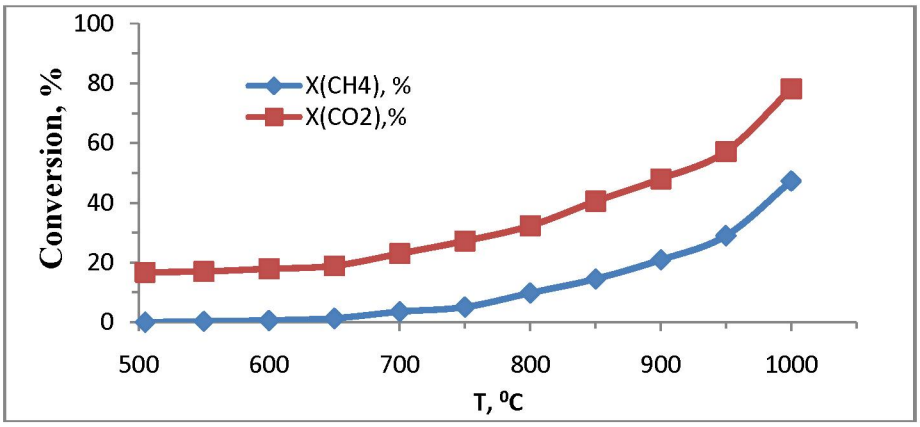

Figure 2 – The effect of temperature on BRM over the 1% Mo/HZSM-P-Al_2O_3 catalyst at CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h^{-1}

Table 3 – Effect of temperature on the products composition in BRM over the 1%Mo/HZSM-P-Al_2O_3 catalyst at CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h^{-1}

t, °C	Conversion, %		H_2/CO	Product yield	
	X_{CH4}	X_{CO2}		Hydrocarbons	Oxygenates
780	9.1	29.0	0.6	C_2H_4, C_6 (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_2 may actively reacts with C_{ads} 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_4 and CO_2 in BRM over the 2%Mo/HZSM-P-Al_2O_3 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_2O_3 catalyst is synthesis gas, the H_2/CO ratio is 1.3.

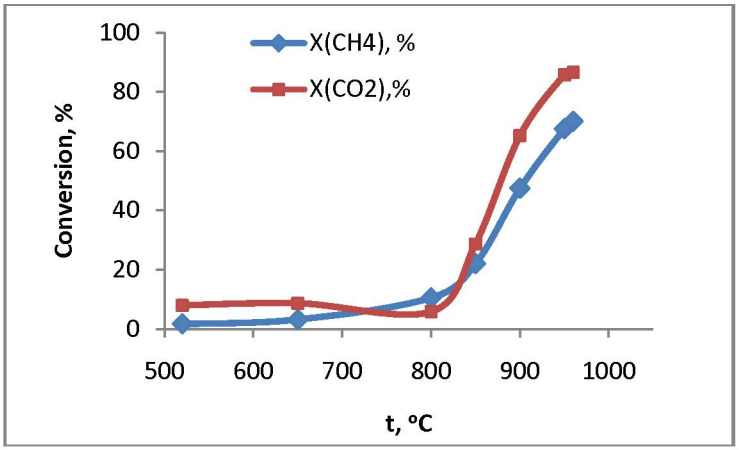

Figure 3 – The effect of temperature on BRM over the 2% Mo/HZSM-P-Al_2O_3 catalyst at CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h^{-1}

At using higher content of Mo – 5 mas.% under the same conditions (CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h^{-1}) an increase in activity of the 5%Mo/HZSM-P-Al_2O_3 catalyst was observed in BRM. Methane conversion became higher than carbon dioxide (Fig. 4): X_{CH4}=82.0%, while X_{CO2}=65.8% at 960°C.

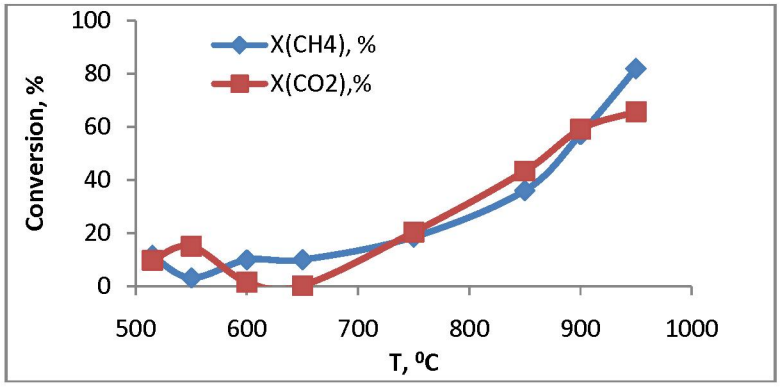

Figure 4 – The effect of temperature on BRM over the 5% Mo/HZSM-P-Al_2O_3 catalyst at CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1 MPa, GHSV=1000h^{-1}

Thus, systematic studies of Mo/HZSM-P-Al_2O_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-Al_2O_3 catalysts in BRM at CH_4:CO_2:H_2O=1.15:1:0.2, P=0.1MPa, t=960°C, GHSV=1000h^{-1}

Mo content, mas.%	Conversion, %	
	X_{CH4}	X_{CO2}
1	47.3	78.2
2	72.4	86.0
5	82.0	65.8

The physicochemical properties of the 2%Mo/HZSM-P-Al_2O_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: MoO_2 (JCPDS, 32-671), η-MoC (JCPDS, 8-384), α-Mo_2C (JCPDS, 35-787), P (JCPDS, 18-964), SiC (JCPDS, 29-1127), Al_2Mo_3C (JCPDS 6-7) were detected by microdiffraction analysis.

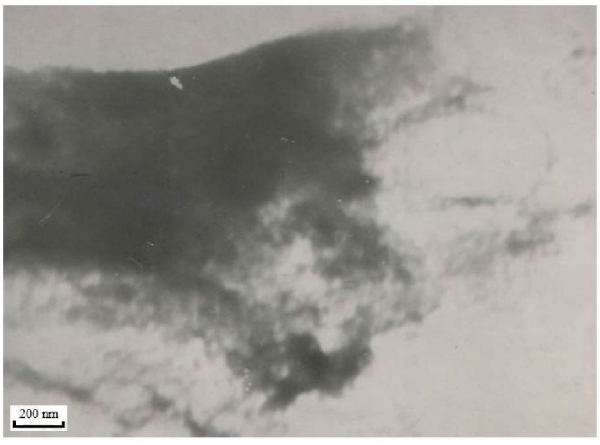

Figure 5 - TEM image of 2%Mo/HZSM-P-Al_2O_3 spent in BRM for 30 hours

It is more important the appearance of molybdenum carbides: MoC and Mo_2C. 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_2O_3 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_2O_3 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_2O_3 catalyst by the BET method showed that some changes occur in the spent sample – S=201.7m^2/g compared to the initial one –S=307m^2/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_2O_3 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_2O_3 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_2O_3 as promising base for manufacturing a cheap stable catalyst for syngas production from methane or biogas by further appropriate modification of the catalyst developed.

Acknowledgement: This research was supported by the Ministry of Education and Science of the Republic of Kazakhstan, the Program # BR05236739 MES RK.

Е.Е. Нурмақанов[1], Г.Д. Закумбаева[1], Ш.С.Иткұлова[1], Л.В. Комашко[1]

[1]АҚ «Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты», Алматы, Қазақстан

ФОСФОР ЖӘНЕ ЦЕОЛИТ ҚОСПАСЫМЕН МОДИФИЦИРЛЕНГЕН Mo/Al_2O_3- КАТАЛИЗАТОРЛАРДАҒЫ МЕТАННЫҢ ТҮРЛЕНУІ

Аннотация. Цеолит (HZSM) және фосфордың қоспаларымен модифицирленген алюминий тотығынан тұратын матрицаға қондырылған Mo-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_2/CO қатынасы бастапқы газ қоспасына су буын қосу есебінен өседі. Сондай-ақ, метанның сусыз риформингі кезінде реакция өнімдерінде C_2, C_6 көмірсутектердің және спирттердің азғантай мөлшері құрайды.

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

УДК 544.478; 542.97; 665.612.3; 546.264-31
МРНТИ 31.15.28

Е.Е. Нурмаканов[1], Г.Д.Закумбаева[1], Ш.С. Иткулова[1], Л.В.Комашко[1]

[1]АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», Алматы, Казахстан

КОНВЕРСИЯ МЕТАНА НА Mo/Al_2O_3 – КАТАЛИЗАТОРАХ, МОДИФИЦИРОВАННЫХ ДОБАВКАМИ ФОСФОРА И ЦЕОЛИТА

Аннотация. Были синтезированы Мо-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_2/CO возрастает при добавлении паров воды в исходную смесь. При сухом риформинге метана в продуктах реакции также содержатся в небольших количествах углеводороды C_2, C_6 и спирты.

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

Information about the authors:

Nurmakanov Y.Y. – D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis, Almaty, Kazakhstan, yerzhan.nurmakanov@gmail.com, https://orcid.org/0000-0002-0404-1833

Zakumbayeva G.D. – D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis, Almaty, Kazakhstan, Academician of NAS RK, Retired, g.d.zakumbaeva@gmail.com, https://orcid.org/0000-0001-5536-2664

Itkulova S.S. – D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis, Almaty, Kazakhstan, s.itkulova@ifce.kz, https://orcid.org/0000-0001-7159-5249

Komasko L.V. – D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis, Almaty, Kazakhstan, komashko535@mail.ru, https://orcid.org/0000-0003-0031-2816

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