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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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SELECTIVE CATALYTIC OXIDATION AND STEAM OXYGEN CONVERSION OF METHANE INTO SYNTHESIS GAS

Abstract. The results of the stability study of the developed dispersed optimal composition Pt-Ru = 1 : 1 (Pt: Ru = 0.7 : 0.3, at.%) of the catalyst in the reaction of selective catalytic oxidation (SCO) and steam oxygen conversion (SOC) of methane into synthesis gas at millisecond contact times are presented. Methods of catalyst regeneration were determined. During the study of the stability of a low-percentage granular sample of 1.0% Pt-Ru/2% Ce/($\theta+\alpha$)Al₂O₃ catalytic system in the process of oxidation of methane, regeneration methods were found that allow stable conduct of the process of SCO and SOC of methane for 410 hours. As a result of the process, a synthesis gas was obtained with a ratio of H₂/CO = 2.0 without the formation of CO₂, which is most suitable for its use in the Fischer-Tropsch synthesis of methanol and hydrocarbons. It is assumed that the reaction of SCO of CH₄ proceeds by a direct mechanism involving reduced Pt⁰, Ru⁰ and Pt-Ru nanoclusters detected by TEM research after testing the stability of the developed Pt: Ru (1:1) catalyst on a carrier.

Keywords: Pt-Ru catalyst, selective catalytic oxidation, steam oxygen conversion, methane, synthesis gas.

Introduction. Synthesis gas is the main raw material for producing a wide range of petrochemical products. Correlation of the ratio of H₂ and CO in the composition of synthesis gas makes it possible to obtain liquid hydrocarbons or oxygenates, CH₃OH, CH₃COOH, CH₂O and C₂H₆O. The process of SCO of methane which proceeds with a molar ratio of hydrogen to carbon monoxide equal to 2.0, could become a reaction, an alternative reaction of steam reforming of methane for the production of synthesis gas. An alternative reaction of steam reforming of methane to obtain syngas can be the process SCO of methane which proceeds with an optimal molar ratio of hydrogen to carbon oxide equal to 2.0.

The creation of large-scale production in natural gas production areas would significantly reduce the cost of target products and reduce environmental pollution. Obtaining a synthesis gas by direct oxidation of CH₄ with a lack of oxygen and millisecond contact times is a relatively new reaction, first performed by M. Pretre, which plays an important role in petrochemical syntheses. Researchers returned to the study of this process in the 90 years thanks to the use of a reactor with block porous catalysts during the process in a micro-reactor when secondary reactions are prevented.

In 1992, Schmidt investigated reduced Pt, Pd, and Rh catalysts in selective catalytic oxidation at an excess of methane, high temperature, and a contact time of 0.01 - 0.004 s to form a synthesis gas with high selectivity for hydrogen and carbon monoxide. Among the studied compositions, the best results were shown on Rh catalysts carried to Al₂O₃ [1-3].

It is known that platinum group metals are more active than Fe, Co, Ni, and are less prone to carbon deposition. Most of the known compositions of catalysts for SCO of methane include noble metals with a content of $\geq 1\%$ of metals in the active phase. To achieve high performance in the production of synthesis

gas in the process of methane co-production at high volume velocity without the formation of CO₂ with a ratio of hydrogen to carbon monoxide equal to 2, the catalyst must provide both a high conversion of methane and selectivity for the target product [4-15].

We studied Pt, Ru, and Pt-Ru/2%Ce/($\theta+\alpha$)-Al₂O₃ catalytic systems with varying Pt to Ru ratios in the reaction of SCO of methane into synthesis gas at millisecond contact times [16-20]. Determined that at contact times of 3.0 - 4.0 millisecond the conversion of methane at 1173K varies from 96 to 100%, the selectivity for hydrogen is 100% and for CO is 95-100%. It was found that 100% conversion of methane by direct mechanism into synthesis gas with 100% selectivity for hydrogen and carbon monoxide was achieved at the atomic ratio Pt : Ru = 2 : 1 or 1 : 1 (32.4 and 45.3 at.% Ru in a mixture of Pt-Ru) and the contact time is 4.0 millisecond. Physical and chemical methods determined that the introduction of ruthenium in a platinum catalytic system with a ratio of metals Pt : Ru = 2 : 1 (0.68 Pt: 0.32 Ru. weight.%) increases oxygen adsorption in the second temperature region, and the surface is stabilized in a uniform state. It is assumed that on Pt: Ru (2:1. 1:1) catalysts, the reaction of SCO of CH₄ proceeds by a direct mechanism with the participation of reduced Pt-Ru clusters that have the greatest ability to absorb atomic hydrogen.

This paper presents data on the stability of the developed Pt-Ru = 1 : 1 (Pt : Ru = 0.7 : 0.3 at.%) catalyst. The activity of the catalyst was studied in the reactions of SCO and SOC of methane into synthesis gas at low contact times. As a result of the conducted research, the methods of catalyst regeneration were determined.

Experimental

Catalyst preparation

Pt-Ru catalysts supported on 2%Ce/($\theta+\alpha$)-Al₂O₃ have been prepared by incipient wetness on ($\theta+\alpha$)-Al₂O₃ (100-200 μm , $S = 57.7 \text{ m}^2/\text{g}$) from water solutions of salts with subsequent heating and reduction with H₂+Ar at 623-1023 K. Tests were carried out in a continuous flow quartz micro reactor by a literature technique.

The activity of the developed catalytic systems in the process SCO of methane was determined in a catalytic flow unit at atmospheric pressure in a quartz microreactor with an internal diameter of 0.45 cm. 10 mg of the catalyst suspension was thoroughly mixed with quartz powder (particle size 0.2 mm in a ratio of 1: 43, height 20 mm). Then, larger quartz particles (1÷2 mm) were added to the reactor from above to a total layer height of 70 mm. After that, the initial reaction mixture was fed under the following conditions: CH₄:O₂:Ar = 2.0 : 1.0 : 97.0. (%) T = 1173K, V = 9·10⁵ h⁻¹, $\tau = 0.004 \text{ s}$. In the process the SOC of methane: CH₄: O₂: H₂O : Ar = 2.0 : 1.0 : 2.0 : 95.0, %, T = 1073 – 1173 K, V = 1·10⁵ - 9·10⁵ h⁻¹.

Characterization techniques

Analysis of the initial mixture and the reaction products was performed using "Chromos GC-1000" (Russia) chromatograph, which was equipped with packed and capillary columns. The packed column is used for the analysis of H₂, O₂, N₂, CH₄, C₂H₆, C₂H₄, C₃-C₄ hydrocarbons, CO and CO₂. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. The speed of the carrier gas Ar is 10 ml / min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve $V = f(S)$ was constructed, where V - amount of substance in ml, S - peak area in cm². Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was $\pm 3.0\%$.

Physico-chemical research

Electron microscopic characteristics of the catalysts were obtained using the EMK-125 K microscope (1990, USSR) at an accelerating voltage of 75 kV. The morphology, particle size and their chemical composition was investigated by increasing to 120,000 times by using the replica technique with extraction with the use of microdiffraction of electrons. Carbon replicas were sprayed in a vacuum universal post, then the catalyst carrier was dissolved in HF. Identification of micro-diffraction patterns was carried out using the jspds card file of 1986.

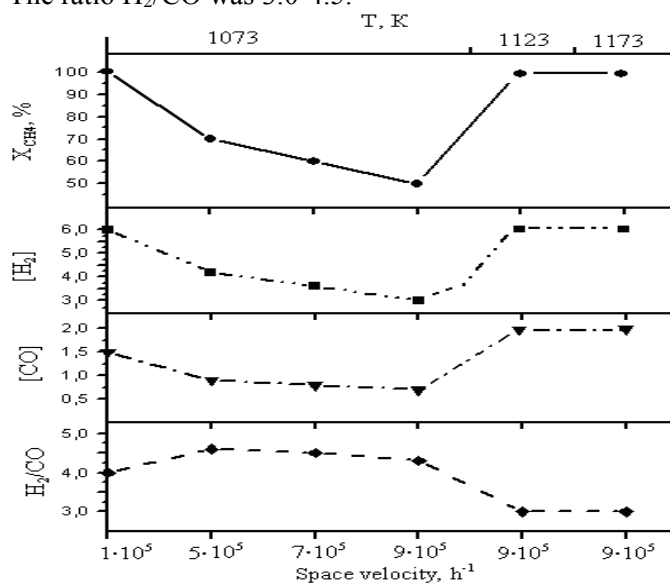
Results and discussion. A priori, it is known that the addition of water vapor to the reaction mixture reduces the formation of carbon on the surface of the catalysts. In modern installations at a pressure of 2 MPa or higher, the residual content of CH₄ after steam conversion is 8-10%. In order to achieve a residual content of methane within 0.5% the conversion is usually carried out in 2 stages. Stage 1: under pressure and stage 2: steam-air conversion in the presence of air oxygen. This results in a sin gas of stoichiometric composition and eliminates the need for separation of products after the reaction.

To study the activity of catalytic systems synthesized by capillary impregnation in the SOC reaction the effect of the concentration of added water vapor in the initial reaction mixture in the SOC was first performed by 2.0% CH₄ + 1.0% O₂ + Ar + H₂O at V = 9·10⁵ h⁻¹, τ = 4,0 ms. It was found that when adding small amounts of water vapor to the reaction system with a ratio of CH₄ : H₂O = 1 : 0.5 with an increase in temperature from 1023 to 1173 K, there was a gradual increase in the conversion of methane from 70 to 90%, S for H₂ from 23.8 at 1023 K to the maximum 100% value at 1173 K, without the formation by-product of a CO₂. The ratio of hydrogen to carbon monoxide vary from 3.3 to 5.0. At higher ratio of CH₄ : H₂O = 1 : 1 with increasing the temperature of reaction from 1023 to 1123 and 1173 K was also observed an increase conversion of methane and selectivity of H₂ respectively, from 97.5% and 18.8 to maximum 100% of the values without the formation of CO₂ with a ratio of H₂/CO from 3.0 to 3.6.

When the added water vapors increased to the ratio CH₄ : H₂O = 1 : 2, as the temperature increased from 1023 to 1123 K, all parameters of process also increased. The conversion of methane and selectivity of hydrogen increased from 62.5 and 26.6 to the maximum 100% values, and the selectivity for CO ranged from 88.8 – 98.2% with the appearance of small amounts of CO₂ in the reaction system (0.013 – 0.023%). As the temperature increased, the H₂/CO ratio decreased from 10.0 to 4.6.

Thus, determined that the preferred process for converting of methane is SOC of CH₄ with a ratio of CH₄ : H₂O = 1 : 1. The addition of 2.0% water to the reaction system increases to the maximum values conversion of methane, selectivity for H₂ and CO (100%) at a temperature 50⁰C lower than at the SCO of methane to produce a synthesis gas with a ratio of H₂/CO = 3.0 without the formation of CO₂.

A study of the effect of changes the volume velocity and temperature of the process SOC of methane CH₄ : O₂ : H₂O : Ar = 2.0 : 1.0 : 2.0 : 95.0,% on the conversion of methane, the concentration of H₂ and CO by the catalytic system 1.0%Pt-Ru (1:1)/2%Ce/(θ+α)-Al₂O₃ at T = 1073 – 1173 K, V = 1·10⁵ - 9·10⁵ h⁻¹. As can be seen from figure 1, the reaction of SOC of methane at 1073 K with an increase the volume velocity from 1·10⁵ h⁻¹ to 9·10⁵ h⁻¹ X_{CH₄}, the concentration of H₂ and CO decreases. However, when the temperature of process increases to 1123 and 1173 K, all the parameters of process increase again to the initial maximum values. The ratio H₂/CO was 3.0-4.5.

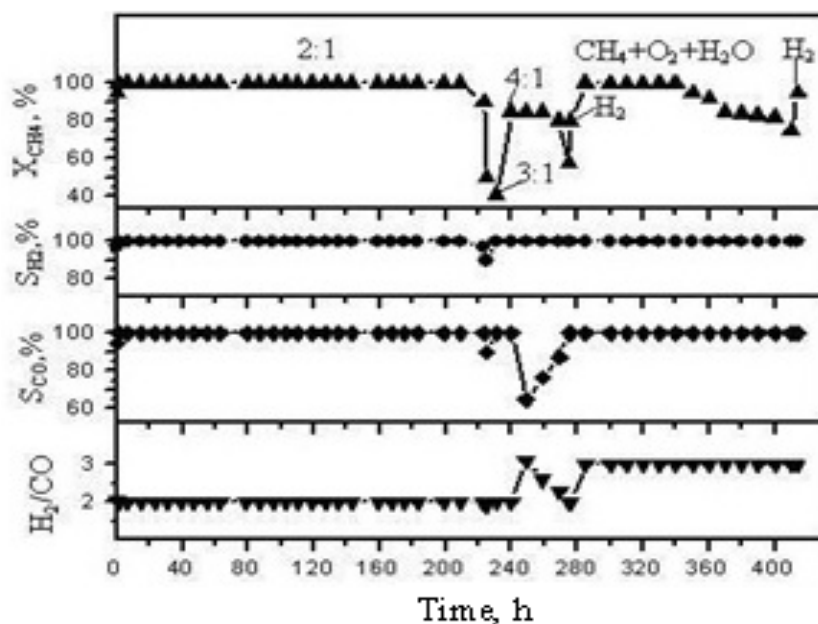


Experimental conditions: SOC of CH₄ : O₂ : H₂O : Ar = 2.0 : 1.0 : 2.0 : 95.0%, T = 1073 – 1173 K, V = 1·10⁵ - 9·10⁵ h⁻¹

Figure 1 - Influence of the volume velocity on change of X_{CH₄}, [H₂], [CO] in the SOC of methane by 1.0%Pt-Ru (1:1)/ 2%Ce/(θ+α)-Al₂O₃

Thus, determined that the process of SOC of methane with the optimum ratio of $\text{CH}_4 : \text{H}_2\text{O} = 1 : 1$ proceeds with complete conversion of the initial methane and maximum selectivity for the main products of the reaction without formation of CO_2 at 1123 K and volume velocity of $9 \cdot 10^5 \text{ h}^{-1}$ and decreasing the temperature of the reaction to 1073 K and volume velocity of $1 \cdot 10^5 \text{ h}^{-1}$ on 1.0%Pt-Ru (1:1)/ 2%Ce/($\theta+\alpha$)- Al_2O_3 catalyst.

It is known that one of the most important characteristics of catalysts is their stability. We tested the stability of the developed optimal composition of Pt-Ru = 1 : 1 of the catalytic system in the processes of SCO and SOC of methane in synthesis gas at low contact times. From the data in figure 2 shows that up to 225 hours the developed catalyst does not lose its activity in the reaction of methane SCO. Then the conversion of methane was gradually reduced and the test was performed with a change in the concentration of the initial reaction mixture at $\text{CH}_4 : \text{O}_2 = 3 : 1$ and $\text{CH}_4 : \text{O}_2 = 4 : 1$.



Condition the process of SCO of methane: $\text{CH}_4 : \text{O}_2 : \text{Ar} = 2.0 : 1.0 : 97.0, \%$, $T = 1173 \text{ K}$, $V = 9 \cdot 10^5 \text{ h}^{-1}$, $\tau = 0.004 \text{ s}$
and SOC of methane $\text{CH}_4 : \text{O}_2 : \text{H}_2\text{O} : \text{Ar} = 2.0 : 1.0 : 2.0 : 95.0, \%$, $T = 1073 \text{ K}$, $V = 1 \cdot 10^5 \text{ h}^{-1}$, $\tau = 0.036 \text{ s}$

Figure 2 – Change conversion of methane, selectivity of H_2 and CO , ratio of H_2/CO on 1.0 % Pt-Ru (1:1)/2%Ce/($\theta+\alpha$) Al_2O_3 catalyst in time

After that updating of catalyst was performed by regeneration in mixture of $\text{H}_2 + \text{Ar}$. Determined that the most optimal is adding in the reaction mixture of water vapors. Then only the activity returned to its starting value. Next, the process of SOC of CH_4 was conducted at the concentration of water vapors found experimentally, which was optimal. It should be noted that in these processes use only 10 milligrams of a catalyst diluted four hundred times with quartz.

Thus, it is established that the developed catalytic system 1.0%Pt-Ru(at. %)/2%Ce/($\theta+\alpha$)- Al_2O_3 selectively works without losing its activity for 414 hours in the reaction of SCO and SOC of methane into synthesis gas.

The following data are presented for 1.0% Pt-Ru catalyst, which is the most active with a ratio of 1 : 1 at a regeneration temperature of 573 K (figure 3). It can be seen that the catalyst contains from phases of both platinum and ruthenium, as well as their oxides, but also with adsorbed platinum and ruthenium by diffractograms, it was determined that bimetallic Pt-Ru nanoclusters are formed. These data indicate that the active catalyst among the compositions studied by us differs in that separate adsorption occurs on the detected Pt-Ru clusters. It is assumed that dissociation of methane can occur on one side of the platinum cluster, and oxygen activation can occur on the other side of the ruthenium cluster.

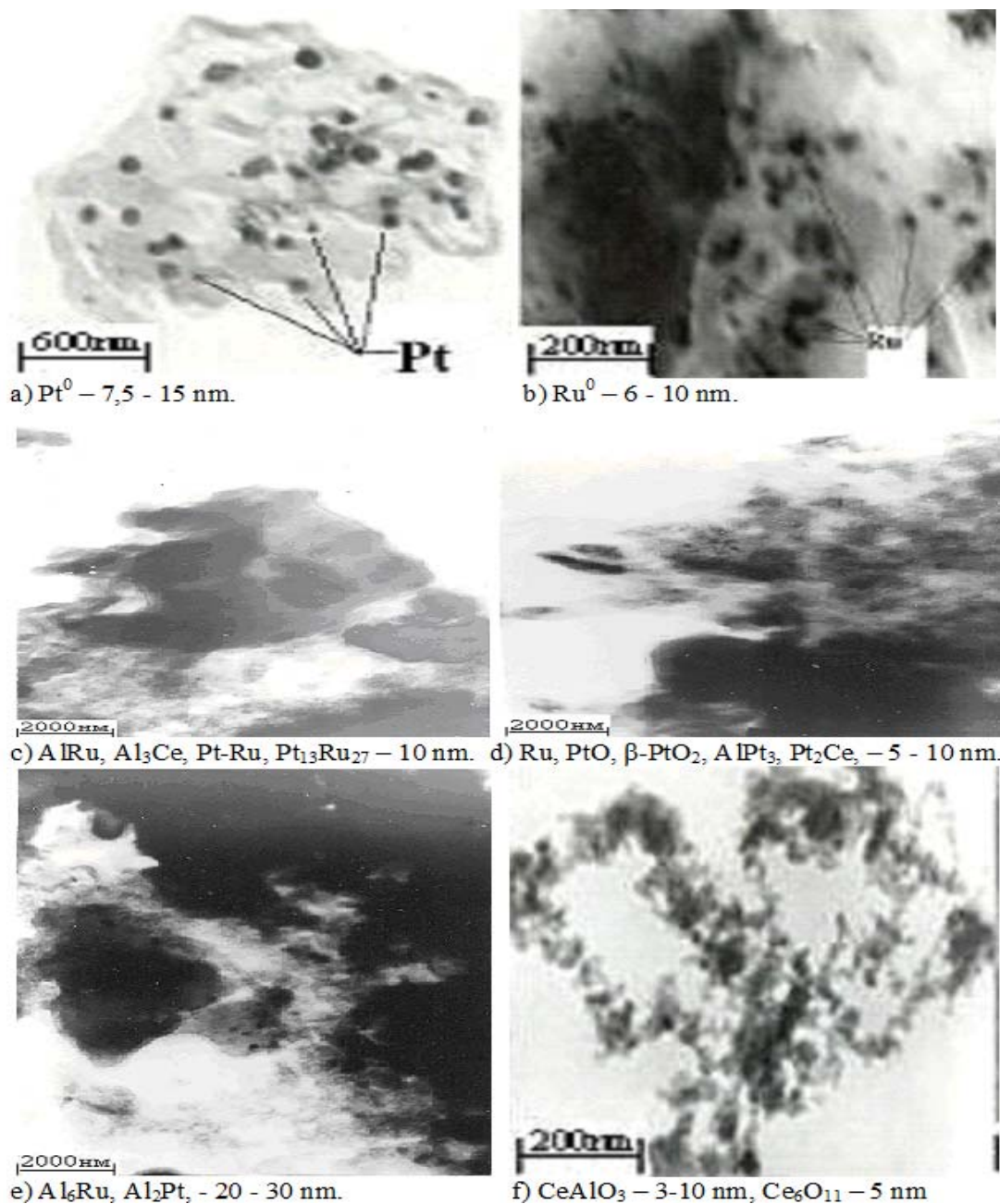


Figure 3 - Electron microscopic photos of various phases reduced in H_2 at 573 K
1.0% Pt-Ru/2%Ce/($\theta+\alpha$)- Al_2O_3 (a, b, c, d, e, f) catalysts

Conclusion. During the study of the stability of a low-percentage granular sample of 1.0% Pt-Ru/2% Ce/($\theta+\alpha$)- Al_2O_3 catalytic system in the process of oxidation of methane, regeneration methods were found that allow stable conduct of the process of SCO and SOC of methane for 410 hours. As a result of the process, a synthesis gas was obtained with a ratio of $H_2/CO = 2.0$ without the formation of CO_2 , which is most suitable for its use in the Fischer-Tropsch synthesis of methanol and hydrocarbons. It is assumed that the reaction of SCO of CH_4 proceeds by a direct mechanism involving reduced Pt^0 , Ru^0 and Pt-Ru nanoclusters detected by TEM research after testing the stability of the developed Pt: Ru (1:1) catalyst on a carrier.

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МЕТАННЫҢ СИНТЕЗ-ГАЗҒА ДЕЙІН СЕЛЕКТИВТІ КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ ЖӘНЕ БУ ОТТЕКТІ КОНВЕРСИЯЛАНУЫ

Аннотация. Синтез-газ мұнай-химия өнімдерінің кең спектрін өндіру үшін негізгі шикізат болып саналады. Синтез-газ құрамындағы H_2 және CO арақатынасының корреляциясы сұйық көмірсутектерді немесе CH_3OH оксигенаттарын, CH_3COOH , CH_2O және C_2H_6O . Синтез-газды алумен метанның бу риформингінің баламалы реакциясы сутегі оксидіне оңтайлы молярлық қатынасына 2,0 тең болатын метанның бөліну үдерісі болуы мүмкін.

Табиғи газ өндіру аудандарында ірі ауқымды өндіріс құру мақсатты өнімнің өзіндік құнын айтарлықтай төмендетуге және қоршаған ортаның ластануын төмендетуге мүмкіндік берер еді. Оттегінің жетіспеуі барысында және контактінің миллисекунд уақытында CH_4 тікелей тотығу жолымен синтез-газды алу мұнай-химия синтезінде маңызды рөл атқаратын M . Претре алғаш рет жүзеге асырған салыстырмалы жаңа реакция болып саналады. Зерттеушілер 90-жылдары бұл үдерісті зерттеуге блок кеуекті катализаторлары бар реакторды микрореактор үдерісі барысында екінші реакциялардың алдын алу барысында пайдалану арқылы назарға алған болатын.

Зерттеу жүргізу үшін $2\%Ce/(\theta+\alpha)-Al_2O_3$ тасымалдағышына қондырылған Pt-, Ru және Pt-Ru каталитикалық жүйелердің сериясы дайындалды. Каталитикалық жүйелер элементтерді тасымалдағышқа $/(\theta+\alpha)-Al_2O_3$ (100 – 200 мкм, $S_{уд} = 57,7 \text{ м}^2/\text{г}$) металл тұздарының алдын ала дайындалған су ерітінділері негізінде $Ce(NO_3)_3 \cdot 6H_2O$, $Ru(OH)Cl_3$ және $H_2PtCl_6 \cdot 6H_2O$ арқылы ауаның ылғал сыйымдылығы бойынша капиллярлы сіңдіру әдісімен жүзеге асып, 873 К 3 сағат бойы ауада біртіндеп кептіріліп, ауада біртіндеп қыздырылады. 10 мг катализатордың үлгісі кварц ұнтағымен мұқият араластырылады (бөлшектер өлшемі 1:43 қатынасында 0,2 мм, қабат биіктігі 20 мм). Содан кейін жоғарыдан реакторға қосылған бөлшектер ірі кварц (12 мм) дейінгі жалпы биіктігі қабатының 70 мм. болатын ұнтақпен жабылады.

Содан кейін микрореакторға метанның талғамды каталитикалық тотығу үдерісінің бастапқы реакциялық қоспасы мынадай жағдайларда жіберіледі: $CH_4:O_2:Ar = 2,0 : 1,0 : 97,0$, (%), $T = 1173\text{K}$, $V = 9 \cdot 10^5 \text{ см}^3/\text{с}$, $\tau = 0,004 \text{ с}$. Метанның бу оттекті конверсия процесін жүргізу кезінде: $CH_4 : O_2 : H_2O : Ar = 2,0 : 1,0 : 2,0 : 95,0$, %, $T = 1073 - 1173 \text{ K}$, $V = 1 \cdot 10^5 - 9 \cdot 10^5 \text{ см}^3/\text{с}$.

Бастапқы реакциялық қоспаны және алынған үдеріс өнімдерін талдау «Хроматэк Кристалл 5000.1» хроматографын пайдалана отырып, «Хроматэк Аналитик 2,5» бағдарламалық қамтамасыз ету арқылы жүргізілді. Жылу өткізгіштігі бойынша детекторы бар диатомитті тасымалдағышта гептадеканның 20% құрамының фазасымен толтырылған капиллярлы баған пайдаланылды. Сынамаларды іріктеу реакция басталған сәттен, 1 минуттан кейін автоматты түрде жүргізілді. Алынған өнімдердің концентрациясы қол жеткізілген калибрлеу графиктері негізінде анықталды.

Катализаторлардың электронды-микроскопиялық сипаттамалары 75 kV үдеткіш кернеу кезінде ЭМК – 125 К (1990, КСРО) микроскопында алынды. Морфологиясы, бөлшектер өлшемі және олардың химиялық құрамы электрондардың микродифракциясын қолдана отырып, экстракциямен реплик әдісімен 120000 есеге дейін ұлғаю барысында зерттелді. Көмір репликалары вакуумдық әмбебап постта шанды, содан кейін катализаторлардың тасымалдаушысы HF-да ерітілді. Микродифракциялық картиналарды идентификациялау 1996 ж. JSPDS картотекасы бойынша жүргізілді.

Pt-Ru = 1 : 1 (Pt : Ru = 0,7 : 0,3, ат.%) катализатордың талғамды каталитикалық тотығу (ТКТ) реакциясында және бу оттекті конверсиясында (БОК) метанның синтез-газға жанасу уақытының миллисекунд кезіндегі зерттеу нәтижелері көрсетілген. Төмен пайыздық түйіршіктелген үлгінің тұрақтылығын зерттеу барысында 1,0% Pt-Ru/2%Ce/(\theta+\alpha)Al₂O₃ каталитикалық жүйенің метанның ТКТ және БОК үдерісінде 410 сағат ішінде тұрақты жүргізуге мүмкіндік беретін регенерациялау тәсілдері анықталды. Үдеріс нәтижесінде $H_2/CO = 2,0$ арақатынасымен CO_2 түзілмей синтез-газ алынды, бұл Фишер-Тропш бойынша метанол мен көмірсутектер синтезінде пайдалануда аса қолайлы екені белгілі. CH_4 -ның ТКТ реакциясы Pt:Ru (1:1) катализатордың тұрақтылығын сынаудан кейін ЭМ зерттеу барысында айқындалған нанокластерлердің қалпына келтірілген Pt⁰, Ru⁰ және Pt-Ru қатысуымен тікелей механизм бойынша өтеді деген болжам жасалды.

Түйін сөздер: Pt-Ru катализаторы, талғамды каталитикалық тотықтыру, бу оттекті конверсия, метан, синтез-газ.

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СЕЛЕКТИВНОЕ КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ И ПАРОКИСЛОРОДНАЯ КОНВЕРСИЯ МЕТАНА В СИНТЕЗ-ГАЗ

Аннотация. Синтез-газ является основным сырьем для производства широкого спектра нефтехимической продукции. Корреляция соотношения H_2 и CO в составе синтез-газа позволяет получать жидкие углеводороды или оксигенаты CH_3OH , CH_3COOH , CH_2O и C_2H_6O . Процесс получения метана, протекающий при молярном соотношении водорода к монооксиду углерода, равном 2,0, может стать реакцией, альтернативной реакции парового риформинга метана для получения синтез-газа. Альтернативной реакцией парового риформинга метана с получением синтез-газа может быть процесс выделения метана, протекающий с оптимальным молярным отношением водорода к оксиду углерода, равным 2,0. Создание крупномасштабного производства в районах добычи природного газа позволило бы значительно снизить себестоимость целевой продукции и снизить загрязнение окружающей среды. Получение синтез-газа путем прямого окисления CH_4 при недостатке кислорода и миллисекундном времени контакта является относительно новой реакцией, впервые осуществленной М. Претре, которая играет важную роль в нефтехимическом синтезе. Исследователи вернулись к изучению этого процесса в 90-е годы благодаря использованию реактора с блочными пористыми катализаторами во время процесса в микрореакторе, когда вторичные реакции предотвращаются.

Для проведения исследований была приготовлена серия Pt-, Ru- и Pt-Ru каталитических систем, нанесенных на $2\%Ce/(\theta+\alpha)-Al_2O_3$. Каталитические системы были приготовлены методом последовательного внесения элементов на носитель $(\theta+\alpha)-Al_2O_3$ (100 – 200 мкм, $S_{уд} = 57,7 \text{ м}^2/\text{г}$) из заранее приготовленных водных растворов солей металлов $Ce(NO_3)_3 \cdot 6H_2O$, $Ru(OH)Cl_3$ и $H_2PtCl_6 \cdot 6H_2O$ методом капиллярной пропитки на воздухе по влагеомкости с последующим постепенным прогревом на воздухе при 873 К 3 ч. Активность разработанных каталитических систем в процессе СКО метана определяли в каталитической проточной установке при атмосферном давлении в кварцевом микрореакторе с внутренним диаметром 0,45 см. 10 мг навеска катализатора тщательно перемешивалась с порошком кварца (размер частиц 0,2 мм в соотношении 1:43, высота слоя 20 мм). Затем сверху в реактор добавлялись частицы более крупного кварца (1÷2 мм) до общей высоты слоя 70 мм. После этого подавалась исходная реакционная смесь при следующих условиях: $CH_4:O_2:Ar = 2,0 : 1,0 : 97,0$, (%), при $T = 1173\text{K}$, $V = 9 \cdot 10^5 \text{ ч}^{-1}$, $\tau = 0,004 \text{ с}$. При процессе ПКК метана: $CH_4 : O_2 : H_2O : Ar = 2,0 : 1,0 : 2,0 : 95,0$, %, $T = 1073 - 1173 \text{ K}$, $V = 1 \cdot 10^5 - 9 \cdot 10^5 \text{ ч}^{-1}$. Анализ исходной реакционной смеси и полученных продуктов процесса проводили с использованием хроматографа «Хроматэк Кристалл 5000.1» с программным обеспечением «Хроматэк Аналитик 2,5», снабженного автоматическим газовым дозатором, подключенным непосредственно к установке по окислению метана в синтез-газ. Использовалась капиллярная колонка, заполненная фазой состава 20% гептадекана на диатомитовом носителе с детектором по теплопроводности. Отбор проб проводился автоматически через 1 минуту после начала реакции. Концентрации полученных продуктов определяли на основе полученных калибровочных графиков. Электронно - микроскопические характеристики катализаторов получены на микроскопе ЭМК – 125 К (1990, СССР) при ускоряющем напряжении 75 кВ. Морфология, размер частиц и их химический состав исследовались при увеличении до 120000 раз методом реплик с экстракцией с применением микродифракции электронов. Угольные реплики напылялись в вакуумном универсальном посту, затем носитель катализаторов растворялся в HF. Идентификация микродифракционных картин проводилась по картотеке JSPDS 1986 г.

В представленной работе приведены данные по изучению стабильной работы разработанной Pt-Ru = 1:1 (Pt:Ru = 0,7:0,3, ат.%) каталитической системы. Активность катализатора исследована в реакции селективного каталитического окисления (СКО) и парокислородной конверсии (ПКК) метана в синтез-газ при малых временах контакта. В процессе исследования стабильности низкопроцентного гранулированного образца $1,0\%Pt-Ru/2\%Ce/(\theta+\alpha)Al_2O_3$ каталитической системы в процессе окисления метана найдены способы регенерации, позволяющие стабильно проводить процесс СКО и ПКК метана в течение 410 часов. В результате процесса получен синтез-газ с соотношением $H_2/CO = 2,0$ без образования CO_2 , что наиболее подходит для его использования в синтезах метанола и углеводородов по Фишеру-Тропшу. Предполагается, что реакция СКО CH_4 протекает по прямому механизму с участием восстановленных Pt^0 , Ru^0 и Pt-Ru нанокластеров, обнаруженных ЭМ исследованием после испытания стабильности разработанного Pt:Ru (1:1) катализатора на носителе.

Ключевые слова: Pt-Ru нанесенный катализатор, селективное каталитическое окисление, парокислородная конверсия, метан, сингаз.

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