



MODERNIZATION OF CATALYST SYSTEMS FOR THE PROCESSES OF HYDROCARBON CONVERSION TO SYNTHESIS GAS

Alena Kuzhaeva, Natalia Dzhevaga and Igor Berlinskii

Saint-Petersburg Mining University, Russian Federation, Saint-Petersburg, Russia

E-Mail: dzhevaga331@mail.ru

ABSTRACT

Synthesis gas is an important intermediate of organic petrochemical synthesis. At this article the features of the catalytic conversion of methane to synthesis gas are described. A review of information on the chemical composition of catalysts is given and assumptions about the mechanism of their action are made. The facts and generalizations contained in the article can be useful in determining ways to improve catalytic systems. The most active and most selective catalytic systems allow optimizing existing processes by reducing energy consumption, cost, emissions and increasing the yield of a valuable product. The effective and rational use of natural and secondary resources is determined by the leading role of catalysis in the implementation of chemical transformations. Increasing the depth of conversion and the integrated use of raw materials, as well as ensuring the environmental cleanliness of the technological processes of its processing is achieved by using highly efficient catalysts.

Keywords: methane conversion, synthesis gas, dispersion, aluminum oxide, platinum, catalysts, carriers, partial pressure.

INTRODUCTION

Synthesis gas is an important feedstock for the production of numerous chemical products. Depending on the hydrogen and carbon monoxide ratio (I) in synthesis gas, it is used for obtaining liquid hydrocarbons and oxygen-containing compounds, including methanol, acetic acid, formaldehyde or dimethyl ether [1-3].

In the industrial environment, carbon monoxide that is part of synthesis gas is consumed mainly for the synthesis of methanol (more than 50%), oxo synthesis products (15%), acetic acid (10-15%). In small amounts, CO is used in herbicide and pharmaceutical production [4-6].

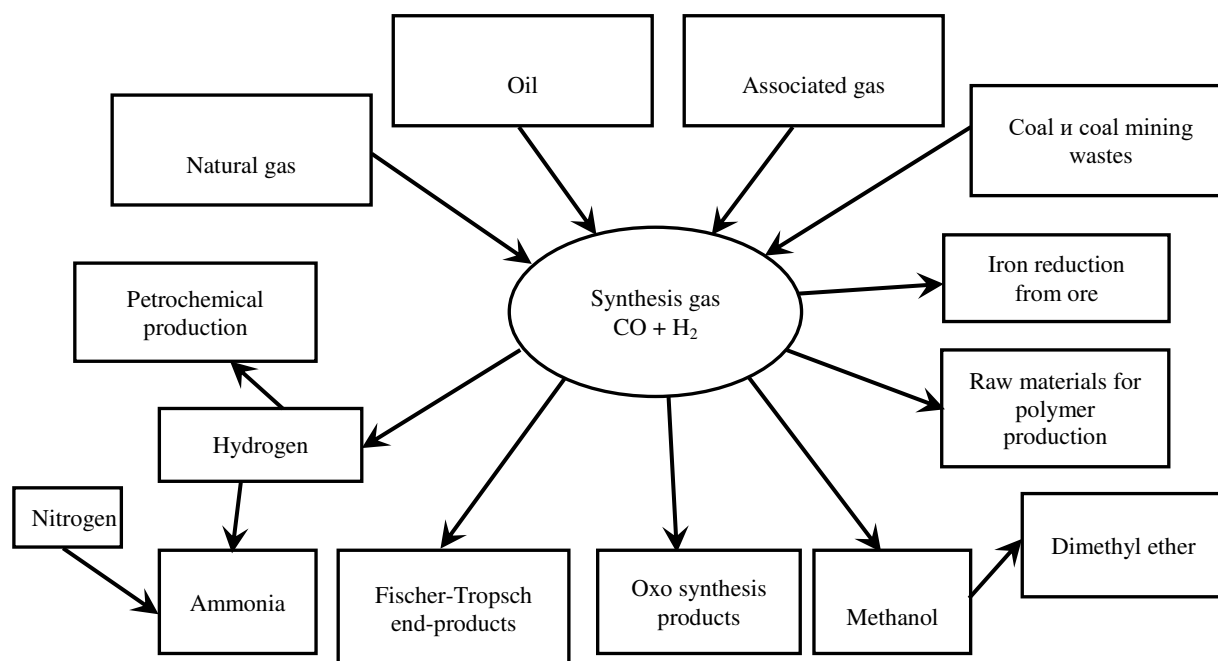


Figure-1. Sources and major application areas of synthesis gas.

Synthesis gas of specific composition is obtained as a result of methane conversion, the sources of which are natural gas and other hydrocarbons. The special attention is given to effective processes of hydrocarbon processing - substrates of synthesis and anthropogenic origin, including substrates obtained from renewable biomass.

The development of methane and carbon dioxide joint processing is of practical concern for the purpose of industrial waste gas carbon and biogas carbon rational use. High thermodynamic stability of CH₄ and CO₂ molecules complicates this task. Nevertheless, the two specified components are among promising non-petroleum



resources for the production of important carbon-bearing products and hydrogen [7].

Table-1. Main petrochemical products from synthesis gas.

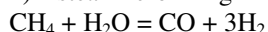
Product	Required ratio H ₂ /CO, mol/mol	Production volume, kt/year	Synthesis gas demand, km ³ /h (normal conditions)
Methanol	2:1	160 – 1,275	48 – 1,900
Acetic acid	0:1	275 - 545	18 - 36
Acetic anhydride	0:1	90	3.5
Oxo synthesis products	2:1	115 - 275	12 - 25
Phosgene	0:1	45 - 160	3.5 - 12
Formic acid	0:1	45	3.5
Methyl formate	0:1	9	0.6
Propionic acid	0:1	45 - 68	2.4 – 3.5
Methyl methacrylate	1:1	45	4.7
1,4-butanediol	2:1	45	4.7

The basic procedure of natural gas processing is steam methane reforming.

Methods of methane oxidative reforming to synthesis gas

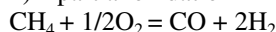
The three methods of methane oxidative reforming to synthesis gas are:

1) steam reforming



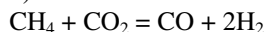
$$\Delta H = +206 \text{ kJ/mole}$$

2) partial oxidation



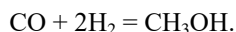
$$\Delta H = -35.6 \text{ kJ/mole}$$

3) carbon dioxide reforming



$$\Delta H = +247 \text{ kJ/mole}$$

Steam reforming method - is the only method that is currently used in industry. The quantitative composition of formed synthesis gas in chemical reactions is different. Demand in synthesis gas of one or another composition is determined by its subsequent industrial use. Thus, for methanol synthesis the synthesis gas with 1:2 ratio is required [8-10]:



For ammonia production from the nitrogen-hydrogen mixture, the synthesis gas with the composition of 1CO: 3H₂ is used on the production stage. Receipt of synthesis gas with the ratio of 1:1 for the industrial production of diethyl ether corresponds to the equation [11, 12]:



However, in the conditions of this process, H₂O interacts with CO (CO steam reforming).

Great difficulties in the practical realization of all methane reforming methods are associated with a significant thermal effect: both the endothermicity of steam and carbon dioxide reforming and the exothermicity of partial oxidation create a problem of heat supply or removal [13-15].

The product composition as it leaves the reformer is usually very close to equilibrium and can be predicted on the assumption of following parameters: a) temperature at the outlet from the apparatus, b) mole ratio of steam/carbon and CO₂/C and c) pressure.

A search for selective catalysts permitting the purposeful receipt of beneficial products is being held for a long time; however, the problem is not yet completely resolved. Therefore, the studies on catalysts, capable of selectively reducing methane, are still topical. To understand the mechanism of the catalytic process and the possibility of its control the knowledge of catalyst surface condition is required. Effective catalyst shall combine not only high activity but also high selectivity in respect to the required product with high formation rate [16, 17], as well as keep both properties throughout its working period [18, 19].

Selectivity shall be understood as the ability of the catalyst to hasten one of the thermodynamically possible reaction paths. A relationship between the reaction rate and the number of products may have a complicated nature due to diffusive and correlated factors, the studying of which presupposes the use of complicated methods [20-23].

Calculations use the differential selectivity S_g that is equal to the ratio of the amount of product that was formed by the instant of time t at this temperature to the total amount of formed products:



$$S_i = \frac{A_i}{\sum A_i}$$

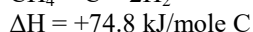
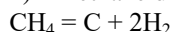
Given that the test conditions involve the equal rate of reagent passing through 1 cm³ of catalyst (the identical volume rate), it is supposed that S_i qualitatively characterizes the CH₄ reduction process selectivity relative to product i.

It should be noted that the use of selectivity when comparing catalyst properties relative to a specific chemical process implies that the reactions relate to a commensurate class [24-27], quasistationary in chemistry terms, otherwise the description loses touch with the physical understanding of time.

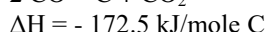
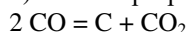
Another important technological aspect relates to the side reactions of carbon formation that may occur when feeding the insufficient amount of water steam to the reforming installation. Coke production primarily deactivates the catalyst, then it causes the destruction of its granules, which in turn results in partial or complete blocking of reaction flow in the catalyst layer that fills out the tube side. As a result, the local overheating sections occur.

The main obstacle to the use of various catalysts for methane reforming is their ease of poisoning by coke. Two paths of carbon formation during methane decomposition are possible [29-31]:

1) methane dissociation



2) CO disproportionation, Boudouard equilibrium



In reality, reactions take place at various temperatures: methane dissociation reactions takes place mainly at high temperatures, Boudouard equilibrium - at low temperatures, and in real condition coke forms almost always. In accordance with thermodynamic considerations, the total carbon deposition shall decrease with temperature rise. The test confirms that the main quantity of carbon forms according to methane dissociation reaction, but not Boudouard equilibrium. Often carbon diffuses to metal forming at the catalyst discharge in the form of filaments.

Disadvantages of different catalysts include the high gas-dynamic resistance to gas flow, imposing restrictions on the rate of volume velocity, and therefore on the synthesis gas output rate, as well as on the increased coke and carbon dioxide formation [32-34].

Methane oxidation methods

They include homogeneous gas-phase oxidation, oxidation in the presence of heterogeneous catalysts, as well as photochemical and electrophilic oxidation [35-37].

Feedstock, namely natural gas and light hydrocarbons, usually contain sulfurous components that shall be removed to prevent reforming catalyst poisoning.

In the conditions that are favourable to obtaining synthesis gas with low H₂/CO ratio, coke formation is much more likely, therefore the steam reforming catalyst shall be resistant to coke formation processes.

One of the problem solving approaches is the conduction of the steam reforming process that is passivated by sulphur [38]. This process implements the idea of "ensemble control" by the constant addition of sulphur that blocks active centres during coke while preserving active centres of methane steam reforming. Such a process requires the careful dosage of sulphurous components and constant control over the performance of their functions. The use of catalysts containing precious metals is effective, since they are characterized by low coking [39, 40].

Our survey is dedicated to use consideration of platinum-based catalysts that is characterized by a number of features, platinum group metals, and some other elements.

Various scientific approaches to methane conversion using catalytic systems

The use of nanostructured systems as catalysts appears to be the most advanced. The active components of such systems contain particles commensurable in terms of dimensions with the range of action of interatomic forces. The physicochemical methods state-of-the-art permits obtaining metals in the form of nanosized powders. The wide practical use of nanopowders for heterogeneous catalysis, namely methane carbon dioxide reforming to synthesis gas, methane and benzene deep oxidation, ammonia synthesis, Fischer-Tropsch process, carbon dioxide hydrogenation to methanol and others, showed that the addition of metal nanopowders to zeolite permits substantially increase the catalyst activity [41-45]. The ease of linear molecule passing to zeolite active centres, having narrow channels, is conditioned by the so-called form-selective properties of mesomicroporous systems.

Zeolites are catalysts for very many acid-base type reactions. In the course of reactant interaction with catalyst acid sites the formation of carbonium ion occurs. The reaction occurring on the catalyst surface is the controlling step of the whole process [46].

The basic requirements to catalyst carriers are their inertness, mechanical strength (abrasion), stability in reaction conditions and physical properties (specific surface, porosity, which is determined by the average pore size and the pore space distribution by radii) [47-49]. The most widespread catalyst carriers that proved their effectiveness are aluminium, silicone, titan and zirconium oxides.

One of the most studied and widely applied in practice catalyst systems is the "platinum on aluminium oxide" system. Nevertheless, the study of the mechanism of its formation is still topical. The traditionally used compound that is the precursor of active component in this system is chloroplatinic acid that is irreversibly sorbed on the aluminium oxide surface. As a result, on the ready-for-surface catalyst, the platinum centres are formed that are



not uniform by their condition: some part is present in the form of disperse metal crystals, another part - in the form of charged clusters that are chemically bound with the carrier (ion platinum Pt°) [1, 2]. One of the methods of handling the task of platinum stabilization in ion condition under the condition of high-temperature catalyst reduction treatment is the use of platinum hydroxo-complexes as precursor compounds. Their advantage is the possibility of strong metal attachment realization at the expense of OH-ligand complex exchange with aluminium oxide surface hydroxyl groups, which in this particular case plays the role of macroligand of some sort.

The main factor preventing the use of platinum hydroxo complex $H_2[Pt(OH)_6]$ for catalyst preparation is its bad solubility in water. The amphoteric nature of compound allows using it as alkaline or acid solution. However in the first case, problems related to the introduction of undesirable cations to catalyst arise, and in the second case - with the platinum hydroxide settling as a result of abrupt pH increase upon acid solution contact of with oxide carrier surface.

At this stage the improvement of carrier production technology happens for optimization of physicochemical properties and modification of the chemical composition of the carrier - aluminium oxide to achieve the following results:

- uniformly-porous system (increased selectivity);
- percentage of 2-6 nm pores is not less than 90 %;
- the total specific volume of pores is 0.6-0.65 cm^3/g ;
- specific surface (200-250 m^2/g) should not change after regeneration - chlorine content (0.9-1.2 %) depends on it;
- Pt content not more than 0.25 % by weight;
- Pt dispersity is not less than 90 %.

The relationship between methane reforming and the temperature was studied for some VIII group metals applied on zirconium dioxide. It is found that the activity changes in the series: Rh, Pt > Ir, Pd > Ru. Thereby platinum may be considered as the most effective as an active component. Content ~0.5% (by weight) Pt was accepted as optimal and long-run tests (1,000 hrs) were performed with this catalyst [28, 31, 50].

Platinum metals in methane carbon dioxide reforming were more active than Fe, Co, Ni, and less exposed to carbon deposition because of lesser carbon solubility in these metals. Carbon dioxide reforming on these metals occurs with significant velocity even at 500 °C. The major and significant obstacle to their wide application is their high cost. Ru and Rh are the most active among all metals, applied on Al_2O_3 , MgO , ZrO_2 [51]. Ruthenium, rhodium and iridium catalysts are poisoned least of all, but their application is also unpromising due to their high cost. The activity was significantly increased by adding very small (0.02%) amounts of Pt, Pd and Ir to $Ni_{0.03}Mg_{0.97}O$ catalyst [52].

The addition of Ru to catalyst increases its activity significantly by the formation of bimetallic nickel-

ruthenium clusters. At that, the more disperse Ni is obtained, facilitating the formation of more reactive carbon [53]. A search for noble metals applied on catalysts is continued. In [54] it is shown that Pt/ZrO_2 , Rh/ZrO_2 and $Rh/\gamma-Al_2O_3$ are active and stable catalysts at 600 °C. The activity of Pt/ZrO_2 catalyst is determined by the accessible perimeter of applied platinum islands. Whereas the activity of Rh/ZrO_2 and $Rh/\gamma-Al_2O_3$ is determined by the total number of rhodium atoms on the surface and thus does not depend on the carrier nature. Pt/SiO_2 activity is significantly lower.

Studies of $CH_4 + CO_2$ mixture reforming on Pt/ZrO_2 catalyst with the addition of molecular oxygen to the reaction system showed the following results [55]. At 3.14% of O_2 and 800 °C the reaction rate increased slightly, but at 550 - 750 °C the rate increased significantly (thrice at 550 °C and 14% of O_2) [56]. At 11% of O_2 the reforming was constant for 30 hrs. In the absence of oxygen, the reforming decreased from 75 to 70%. It is believed that ZrO_2 facilitates CO_2 dissociation permitting the removal of carbon, resulting from CH_4 dissociation

In paper [57] the carbon dioxide reforming of CH_4 on platinum applied on TiO_2 , ZrO_2 , Cr_2O_3 and SiO_2 was studied. It was established that at 400 - 450 °C the Pt/SiO_2 and Pt/Cr_2O_3 catalysts deactivated rapidly, whereas Pt/ZrO_2 and Pt/TiO_2 catalysts preserved stability for 80 - 100 hrs. According to data of different physical methods, including diffuse scattering IR-spectroscopy, carbon deposition on these catalysts is suppressed. On the Pt/TiO_2 catalyst the effect of "metal-carrier strong interaction" is observed. Big ensembles of Pt atoms are active with respect to carbon deposition; deactivation is removed in the presence of TiO_2 . Obviously, active centres are located at the boundary of Pt and TiO_2 . In the temperature-programmed hydrogenation of carbon deposits on Pt/SiO_2 a broad peak at 600 - 800 °C is registered, on Pt/Cr_2O_3 a narrower peak at 900 °C, on Pt/TiO_2 a very small peak at 200 °C, and on Pt/ZrO_2 no peak is registered.

From studied results, one can draw a conclusion that catalysts in which metal is applied on oxides that are fixed composition phases deactivate rapidly, while the use of variable composition phases prevents catalyst deactivation, probably due to oxygen exchange at the phase boundary: gas-solid solution.

Chemical nature of carriers influences the catalyst activity and selectivity. The carrier nature mainly influences the crystal size and absorption heat, thereby influencing reaction parameters. There is information in accordance with which at the identical dispersity and selectivity the reaction is affected by the carrier acidity. Depending on differential carrier acidity, i.e. the ratio of Brønsted and Lewis sites, catalysts showing different activity and selectivity are formed. The acid function of the carrier controls the formation of the metal active surface [58, 59].



The main directions of improving the efficiency of catalytic systems

To improve the catalyst system characteristics the following measures are proposed:

- improvement of platinum ion (non-metal) share. As a result, the platinum activity in aromatization reactions increases 10-fold;
- Pt dilution by palladium (hydrogenolysis decrease);
- carrier surface treatment for the purpose of increasing its defect structure and obtaining "layered" platinum on it.

The applied catalysts are necessary for metal dispersity increase for the acquisition of catalyst with more developed surface concurrently with small particles stabilization to prevent particle agglomeration.

From the studied Ni-, Rh-, Pt- and Ru- catalysts, applied on various carriers, the Ni/SiO₂ and Rh/Al₂O₃ appeared to be the most active [60, 61]. Low and medium temperature (400 - 800 °C) carbon dioxide reforming of CH₄ was performed on Co, Ni, Ru, Rh, Ir and Pt catalysts, applied on SiO₂ and Al₂O₃ [62]. At 500 °C deactivation was observed only on Ir catalysts. At 800 °C deactivation because of agglomeration was registered on some catalysts; the Ni, Co and Rh catalysts are the most stable. In terms of activity the studied catalysts form the following series: Rh > Ni > Ir > Ru > Pt > Co. Catalysts with SiO₂ carrier are much less active [63-66].

The velocity of carbon dioxide methane reforming is proportional to CH₄ pressure raised to the power of one, while the p_{CO}ⁿ value appears in kinetic equations, specified in various papers, in numerator and denominator raised to the power of n from 0 to 2 [67]. This indicates that methane interaction with the catalyst is the controlling step.

The comparative analysis of acid-base properties of titanium oxide, zirconium oxide, aluminium oxide and ferric phosphate surfaces with catalytic activity in papers [23, 68] showed that the substrate replacement and the method of its treatment (by water or organic solvent) permits changing the reaction direction. Modifiers with high molecular weight exercise the maximum influence on the carrier.

Activities of ruthenium catalysts on the carrier at natural gas complete oxidation changes as follows: Ru/Al₂O₃ > Ru/TiO₂ > Ru/SiO₂ > > Ru/ZrO₂. When studying the catalyst consisting of ruthenium chloride, applied on silica gel, the reduction of CO yield is discovered that can be explained by the chloride ion impact on ruthenium state (at 600 °C - S(CO₂) selectivity = 100 %, and K(CH₄) reforming = 0.52). Therefore, this catalyst can be characterized as more selective than metal ruthenium on SiO₂, but less perspective than Ru on Al₂O₃ [22, 69].

The represented analysis implies that the potential of applied systems was almost exhausted. However, as the adduced material shows, variable composition oxides, used as carriers, prevent catalyst clogging due to

carbonization processes and this line of studies are still prospective. Probably the new generation of catalysts based on the Ni-(Co)-Mo-S system also demonstrates their potential including the strength of surface nonstoichiometric compounds.

More recently a keen interest was shown in nanocrystalline (nanostructured) space structure systems that determine macroscopic ensembles of small particles up to several nanometres in size, coupled together in a certain way. Properties of such materials are determined by both structural features of separate particles and their collective behavior, depending on the character of interactions between particles. At that the crystal lattice of separate particles can be regular, defect and/or elastically stressed. The coupling of separate elements can be realized via intercrystalline boundaries that may have a different structure: quasi-amorphous, highly distorted crystal structure or with misfit dislocations, such as transition layer with other chemical composition, interphase boundaries.

CONCLUSIONS

In literature, special attention is paid to the development of new methods of synthesis of various nanostructured materials, including catalysts. The studies of nanophase structures and their boundaries, electronic and atomic structure are performed.

For a long time, the primary reason for using metals in finely dispersed condition was the optimization of their use by increasing the surface/volume ratio (catalytic reactions occur on surface sites). However, later it was found that the transition to nanosized metal particles may cause changes in specific catalytic activity that is determined as a reaction rate in the presence of a catalyst, per the number of surface (available) atoms of metal. This refers to the emergence of size effect in structure-sensitive catalytic reactions, the rate of which as opposed to structure-insensitive reactions changes with the change of active component mean particle size. The study of size effects is impossible without:

- development of controlled and reproduced methods of metal nanosized particles synthesis with uniform and varied particle distribution by size;
- development of methods for reliable characterization of nanosized particles and determination of their distribution by size;
- study of catalytic properties and the comparison of specific catalytic activity values depending on the mean particle size of applied metal particles;
- study of electronic, structure and adsorptive properties of nanosized metal particles depending on their sizes.

The progress in determination of factors, stipulating the emergence of size effects and the use of new synthesis methods for obtaining catalysts with tightly controlled properties permits obtaining more active (specified particle size) and more selective (uniform



distribution of particles by size) catalysts, thereby permitting the optimization of existing processes in terms of energy consumption reduction (reaction temperature) and price indicators (decrease of noble metals load), the decrease of hazardous emission amount and the increase of valuable product yield.

REFERENCES

- [1] Papavasiliou J., Paxinou A., Słowik G., Neophytides S., Avgouropoulos G. 2018. Steam reforming of methanol over nanostructured Pt/TiO₂ and Pt/CeO₂ catalysts for fuel cell applications. *Catalysts*. 8(11): article № 544.
- [2] Liu D., Men Y., Wang J., Kolb G., Liu X., Wang Y., Sun Q. 2016. Highly active and durable Pt/In₂O₃/Al₂O₃ catalysts in methanol steam reforming. *International Journal of Hydrogen Energy*. 41(47): 21990-21999.
- [3] Wang, F., Li, W.-Z., Lin, J.-D., Chen, Z.-Q., Wang, Y. 2018. Crucial support effect on the durability of Pt/MgAl₂O₄ for partial oxidation of methane to syngas. *Applied Catalysis B: Environmental*. 231, pp. 292-298.
- [4] Schaber V.M., Ivanova I.V. 2017. Prospects for Development of Fuel Cells. *Journal of Mining Institute*. 227: 540-546.
- [5] Vita A., Italiano C., Ashraf M.A., Pino L., Specchia S. 2018. Syngas production by steam and oxy-steam reforming of biogas on monolith-supported CeO₂-based catalysts. *International Journal of Hydrogen Energy*. 43(26): 11731-11744.
- [6] Elsayed N.H., Roberts N.R.M., Joseph B., Kuhn J.N. 2016. Comparison of Pd-Ni-Mg/Ceria-Zirconia and Pt-Ni-Mg/Ceria-Zirconia Catalysts for Syngas Production via Low Temperature Reforming of Model Biogas. *Topics in Catalysis*. 59(1): 138-146.
- [7] Krilov O.V. 2000. Carbon dioxide conversion of methane to syn-gas. *Russian chemical journal*. (1): 19-33.
- [8] Wichert, M., Zapf, R., Ziogas, A., Kolb, G., Klemm, E. Kinetic investigations of the steam reforming of methanol over a Pt/In₂O₃/Al₂O₃ catalyst in microchannels (2016) *Chemical Engineering Science*, 155, pp. 201-209.
- [9] Tahay P., Khani Y., Jabari M., Bahadoran F., Safari N. 2018. Highly porous monolith/TiO₂ supported Cu, Cu-Ni, Ru and Pt catalysts in methanol steam reforming process for H₂ generation. *Applied Catalysis A: General*. 554, pp. 44-53.
- [10] Vass Á., Pászti Z., Bálint S., Németh P., Szíjjártó G.P., Tompos A., Tálas E. 2016. Structural evolution in Pt/Ga-Zn-oxynitride catalysts for photocatalytic reforming of methanol. *Materials Research Bulletin*. 83, pp. 65-76.
- [11] Dybkjaer J., Hansen J.B. Proc. IV Int. 1997. Natural Gas Conversion Symp. Kruger National Park, South Africa, 1995. Amsterdam: Elsevier. pp. 99-116.
- [12] Pashkevich M.A., Matveeva V.A., Danilov A.S. 2019. Migration of pollutants from the mining waste disposal territories on the Kola Peninsula. *Gornyi Zhurnal*. (1): 17-21.
- [13] Pena M.A., Gomer J.P., Fierro J.L.G. 1996. New catalytic routes for syngas and hydrogen production *Appl. Catal.* A144(1-2): 7-57.
- [14] Ioannides T., Verykios X.E. Proc. V Eur. 1997. Workshop on Methane Activation. Limerik. Ireland.
- [15] Krylov O.V., Mamedov A.Kh., Mirzabekova S.R. 1998. Interaction of carbon dioxide with methane on oxide catalysts. *Catal. Today*. 42(3): 211-215.
- [16] Romanovskiy B.V. Basics of Chemical Kinetics. Moscow, Exam, 2006, 415 p.
- [17] Kazakova G.D., Kozlova L.V., Mardashev Yu. S. 1999. The dependence of the selectivity of deposited copper catalysts for oxidation of methane to formaldehyde on the nature of the initial salts and the carrier. *Russian Journal of Physical Chemistry A*. 73(11): 1737-1740.
- [18] Vass Á., Pászti Z., Bálint S., Németh P., Tompos A., Tálas E. 2017. Structural transformation of Ga₂O₃-based catalysts during photoinduced reforming of methanol. *Materials Research Bulletin*. 95, pp. 71-78.
- [19] Palma V., Ruocco C., Ricca A. 2018. Oxidative steam reforming of ethanol in a fluidized bed over CeO₂-SiO₂ supported catalysts: effect of catalytic formulation. *Renewable Energy*. 125, pp. 356-364.
- [20] Гришина М.А., Мардашев Ю.С., Горячева В.Н. Каталитические системы на основе металлических катализаторов в реакции окисления метана. *Инженерный журнал: наука и инновации*, 2013, вып. 6. URL:



- <http://engjournal.ru/catalog/fundamentals/chem/794.html>.
- [21] Timonova O.A., Kamenev A.V., Kaziev G.Z., Mardashev Yu.S. 2008. Enhancement of the efficiency of the process of mild catalytic oxidation of methane. *Petroleum Chemistry*. 48(4): 322-323.
- [22] Dosumov K.D., Popova N.M., Baizhumanova T.S., Tungatarova S.A. 2010. Selective oxidation of methane into synthesis gas at short contact times on low-loading platinum-ruthenium catalysts. *Petroleum Chemistry*. 50(6): 455-461.
- [23] Grishina MA, Mardashev Yu. S. 2012. Prospects for the industrial use of methane oxidation reactions. *Integrated Scientific Journal*. (3): 71-73.
- [24] Timonova O.A., Mardashev Yu.S. 2007. Inversion in selectivity of the methane oxidation under the influence of the support. *Russian Journal of General Chemistry*. 77(12): 2214.
- [25] Timonova O.A., Ivannikov D.I., Mardashev Yu. S. 2009. Accounting for the "inflation" factor in the process of methane oxidation in a flow-through circulation system. *News of universities. Chemistry and chemical technology*. 52(4): 116-117.
- [26] Elsayed N.H., Maiti D., Joseph B., Kuhn J.N. 2018. Precious Metal Doped Ni-Mg/Ceria-Zirconia Catalysts for Methane Conversion to Syngas by Low Temperature Bi-reforming. *Catalysis Letters*. 148(3): 1003-1013.
- [27] Itkulova S.S., Nurmakanov Y.Y., Kussanova S.K., Boleubayev Y.A. 2018. Production of a hydrogen-enriched syngas by combined CO₂-steam reforming of methane over Co-based catalysts supported on alumina modified with zirconia. *Catalysis Today*. 299, pp. 272-279.
- [28] 2000. Achievements in the production of syn-gas, Oostercamp P., Wagner A., Ross Dzh., *Russian chemical journal*. 44(1): 34-42.
- [29] Nikolaeva N., Aleksandrova T., Romashev A. 2018. Effect of grinding on the fractional composition of polymineral laminated bituminous shales. *Mineral Processing and Extractive Metallurgy Review*. 39(4): 231-234.
- [30] Van den Oosterkamp P.F., Chen Q. 1995. Overwater J.A.S. e.a. *Proc. Conf. Large Chemical Plants*. p. 435.
- [31] Seshan K. 1994. Ten Barge H.W., Hally W. e. a. *Ibid*. 81: 285.
- [32] Zhao W., Chizallet C., Sautet P., Raybaud P. 2019. Dehydrogenation mechanisms of methyl-cyclohexane on γ -Al₂O₃ supported Pt13: Impact of cluster ductility. *Journal of Catalysis*. pp. 118-129.
- [33] Yang E., Jang E.J., Lee J.G., Yoon S., Lee J., Musselwhite N., Somorjai G.A., Kwak J.H., An K. 2018. Acidic effect of porous alumina as supports for Pt nanoparticle catalysts in: N -hexane reforming. *Catalysis Science and Technology*. 8(13): 3295-3303.
- [34] Liu S., Tamura M., Shen Z., Zhang Y., Nakagawa Y., Tomishige K. 2018. Hydrogenolysis of glycerol with in-situ produced H₂ by aqueous-phase reforming of glycerol using Pt-modified Ir-ReOx/SiO₂ catalyst. *Catalysis Today*. 303, pp. 106-116.
- [35] Nikitenko S.I., Chave T., Goff X.L. 2018. Insights into the Photothermal Hydrogen Production from Glycerol Aqueous Solutions over Noble Metal-Free Ti-TiO₂ Core-Shell Nanoparticles. *Particle and Particle Systems Characterization*. 35(10): article № 1800265.
- [36] Tálas E., Pászti Z., Korecz L., Domján A., Németh P., Szíjjártó G.P., Mihály J., Tompos A. 2018. PtO_x-SnO_x-TiO₂ catalyst system for methanol photocatalytic reforming: Influence of cocatalysts on the hydrogen production. *Catalysis Today*. 306, pp. 71-80.
- [37] Mills A., Bingham M., O'Rourke C., Bowker M. 2019. Modelled kinetics of the rate of hydrogen evolution as a function of metal catalyst loading in the photocatalysed reforming of methanol by Pt (or Pd)/TiO₂ *Journal of Photochemistry and Photobiology A: Chemistry*. 373, pp. 122-130.
- [38] Dibbern H.C., Olesen P. 1986. Rostrup-Nielsen J. e. a. *Hydrocarbon Processing*.
- [39] Zhao Z., Zhang L., Tan Q., Yang F., Faria J., Resasco D. 2019. Synergistic bimetallic Ru-Pt catalysts for the low-temperature aqueous phase reforming of ethanol. *AIChE Journal*. 65(1): 151-160.
- [40] Ruocco C., Meloni E., Palma V., van Sint Annaland M., Spallina V., Gallucci F. 2016. Pt-Ni based catalyst for ethanol reforming in a fluidized bed membrane reactor. *International Journal of Hydrogen Energy*. 41(44): 20122-20136.



- [41] Dai R., Zheng Z., Sun C., Li X., Wang S., Wu X., An X., Xie X. 2018. Pt nanoparticles encapsulated in a hollow zeolite microreactor as a highly active and stable catalyst for low-temperature ethanol steam reforming. *Fuel*. 214, pp. 88-97.
- [42] Li S., Tuel A., Meunier F.J. 2015. Platinum nanoparticles entrapped in zeolite nanoshells as active and sintering-resistant arene hydrogenation catalysts. *J. Catal.* 332, pp. 25-30.
- [43] Dai C., Zhang S., Zhang A., Song C., Shi C., Guo X. 2015. Hollow zeolite encapsulated Ni-Pt bimetallics for sintering and coking resistant dry reforming of methane. *J. Mater. Chem. A*. 3, pp. 16461-8.
- [44] Shi J., Li X., Wang Q., Zhang Y., Tang Y. 2012. Platinum-encapsulated zeolitically microcapsular catalyst for one-pot dynamic kinetic resolution of phenylethylamine. *J. Catal.* 291, pp. 87-94.
- [45] Zheng Z., Yang D., Li T., Yin X., Wang S., Wu X., *et al.* 2016. A novel BEA-type zeolite core-shell multiple catalyst for hydrogen-rich gas production from ethanol steam reforming. *Catal. Sci. Technol.* 6, pp. 5427-39.
- [46] Ruocco C., Palma V., Ricca A. 2018. Experimental and kinetic study of oxidative steam reforming of ethanol over fresh and spent bimetallic catalysts. *Chemical Engineering Journal*. 10.1016/j.cej.2018.08.164.
- [47] Pastor-Pérez L., Sepúlveda-Escribano A. 2017. Low temperature glycerol steam reforming on bimetallic PtSn/C catalysts: On the effect of the Sn content. *Fuel*. 194, pp. 222-228.
- [48] Yan Y., Zhang Y., Jiang T., Xiao T., Edwards P.P., Cao F. 2017. Glycerol hydrogenolysis over a Pt-Ni bimetallic catalyst with hydrogen generated: In situ. *RSC Advances*. 7(61): 38251-38256.
- [49] Soares A.V.H., Perez G., Passos F.B. 2016. Alumina supported bimetallic Pt-Fe catalysts applied to glycerol hydrogenolysis and aqueous phase reforming. *Applied Catalysis B: Environmental*. 185, pp. 77-87.
- [50] Surendar M., Sagar T.V., Raveendra G., Ashwani Kumar M., Lingaiah N., Rama Rao K.S., Sai Prasad P.S. 2016. Pt doped LaCoO₃ perovskite: A precursor for a highly efficient catalyst for hydrogen production from glycerol. *International Journal of Hydrogen Energy*. 41(4): 2285-2297.
- [51] Oliveira É.V., Seixas A.C.M., Jordão E. 2017. Performance of Pt and Pt-Rh catalyst in the hydrogen production from glycerol. *Canadian Journal of Chemical Engineering*. 95(10): 2018-2023.
- [52] Erdohelyi A., Fodor K., Solymosi F. 1995. Proc. IV Int. National Gas Conversion Symp. Kruger National Park, South Africa. Amsterdam: Elsevier. 1997, pp. 525-530.
- [53] Crisafulli C., Scire S. 1999. Maggiore R. *et al.* *Catal. Lett.* 59(1): 21-26.
- [54] Bitter J.H., Seshan V. 1997. Lercher J.A. *J. Catal.* v. 171, № 1, p. 279 - 286; 1998, v. 176, № 1, pp. 93-101.
- [55] Pendem C., Sarkar B., Siddiqui N., Konathala L.N.S., Baskar C., Bal R. 2018. K-Promoted Pt-Hydrotalcite Catalyst for Production of H₂ by Aqueous Phase Reforming of Glycerol. *ACS Sustainable Chemistry and Engineering*. 6(2): 2122-2131.
- [56] O'Connor A.M. 1997. Ross J.R.H. Abstr. 5th European Workshop on Methane Activation. Linerik, Ireland.
- [57] Bradford M.C.J. 1998. Vannice M.A. *J. Catal.* 173(1): 157-171.
- [58] Palma V., Ruocco C., Meloni E., Gallucci F., Ricca A. 2018. Enhancing Pt-Ni/CeO₂ performances for ethanol reforming by catalyst supporting on high surface silica. *Catalysis Today*. 307, pp. 175-188.
- [59] Palma V., Ruocco C., Meloni E., Ricca A. 2018. Oxidative reforming of ethanol over CeO₂-SiO₂ based catalysts in a fluidized bed reactor. *Chemical Engineering and Processing: Process Intensification*. 124, pp. 319-327.
- [60] Seretis A., Tsiakaras P. 2016. Aqueous phase reforming (APR) of glycerol over platinum supported on Al₂O₃ catalyst. *Renewable Energy*. 85, pp. 1116-1126.
- [61] Safieva R.Z., Stavitskaya A.V., Safieva E.O., Aleksandrova T.N. 2017. Hydrogenation of Unsaturated Hydrocarbons on Pt and Pd Catalysts Encapsulated in Mesoporous Bakelites. *Chemistry and Technology of Fuels and Oils*. 53(4): 455-463.



- [62] Sodesava T. 1998. Kinetics and catalysis. 40(3): 452-453.
- [63] Ribao P. 2018. Alexandra Esteves, M., Fernandes, V.R., Rivero, M.J., Rangel, C.M., Ortiz, I. Challenges arising from the use of $\text{TiO}_2/\text{rGO}/\text{Pt}$ photocatalysts to produce hydrogen from crude glycerol compared to synthetic glycerol. International Journal of Hydrogen Energy, doi.org/10.1016/j.ijhydene.2018.09.148.
- [64] Palma V., Ruocco C., Meloni E., Ricca A. 2017. Highly active and stable $\text{Pt-Ni}/\text{CeO}_2\text{-SiO}_2$ catalysts for ethanol reforming. Journal of Cleaner Production. 166, pp. 263-272.
- [65] Greluk M., Słowik G., Rotko M., Machocki A. 2016. Steam reforming and oxidative steam reforming of ethanol over $\text{PtKCo}/\text{CeO}_2$ catalyst. Fuel. 183, pp. 518-530.
- [66] Majrik K., Pászti Z., Korecz L., Trif L., Domján A., Bonura G., Cannilla C., Frusteri F., Tompos A., Tálas E. 2018. Study of $\text{PtO}_x/\text{TiO}_2$ photocatalysts in the photocatalytic reforming of glycerol: The role of co-catalyst formation. Materials. 11(10), article № 1927.
- [67] Bradford M.C.J. 1999. Vannice M.A. Catal. Revs. 41(1): 1-42.
- [68] Buffoni I.N., Gatti M.N., Santori G.F., Pompeo F., Nichio N.N. 2017. Hydrogen from glycerol steam reforming with a platinum catalyst supported on a $\text{SiO}_2\text{-C}$ composite. International Journal of Hydrogen Energy. 42(18): 12967-12977.
- [69] Bossola F., Pereira-Hernández X.I., Evangelisti C., Wang Y., Dal Santo V. 2017. Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol. Journal of Catalysis. 349, pp. 75-83.