

Conversion of natural gas in the process of steam reforming via aerosol nanocatalysis technology

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Natural gas conversion is the main industrial method to obtain synthetic gas (syngas) in the production of ammonia, alcohol, acids, Fischer–Tropsch synthesis and other organic products. The present study deals with the conversion of natural gas using aerosol nanocatalysis (AnC) of different parameters and their effect on the products. A new technology of obtaining syngas has been approved. In this technology, many catalysts were used such as Fe₂O₃, K-902 D2, GIAP-8, Co₂O₃ and NiO. The optimal result was obtained with NiO. The experimental setup is very flexible to change from one condition to another. By using different parameters, a different ratio of products could be obtained.

Introduction

Natural gas is a petroleum subcategory a complex mixture of hydrocarbons with a minor content of inorganic compounds. Geologists and chemists agree that petroleum originates from plant and animal remains that accumulate on the sea/lake floor along with the sediments that form sedimentary rocks. The processes by which the parent organic material is converted into petroleum are not understood [1].

The contributing factors are thought to be bacterial action, shearing pressure during compaction, heat, and natural distillation at depth, the possible addition of hydrogen from deep-seated sources, and the presence of catalysts [1]. Methane is the major component of the gas mixture. The inorganic compounds such as nitrogen, carbon dioxide, and hydrogen sulfide are not desirable because they are not combustible and cause corrosion and other problems in gas production and processing systems [1].

Clean energy and alternative energy have become the major areas of research worldwide for sustainable energy development. Therefore, one of the most important research and development areas is syngas production. Research and technology development on syngas production has a great potential in addressing three major challenges in the energy area:

- to supply more clean fuels to meet the increasing demands for liquid and gaseous fuels;
- to increase the efficiency of energy utilization for fuels;
- to eliminate the pollutants and decouple the link between energy utilization and greenhouse gas emissions in end-use systems [2].

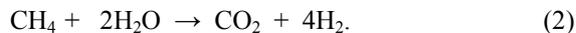
Methane reacts with steam in the presence of a nickel catalyst to produce a CO and H₂ mixture (syngas) represented in equation (1). This reaction is also referred to as SMR and is a widely practiced technology for industrial production of H₂. However, the SMR is not the only reaction as indicated in equation (1) but involves

also contributions from several different catalyzed reactions such as water–gas shift.

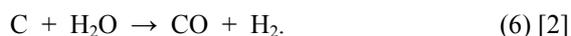
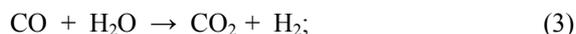
The reaction of methane conversion includes the following:



Also, there is a chance to get an additional quantity of hydrogen:

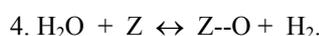
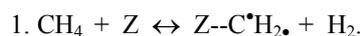


In addition, the following reactions can occur:



In the case of ammonia production, it would be required to obtain the maximum quantity of hydrogen; therefore, reaction (2) would be useful [3]; however in the production of methanol the matter would be different: its better to use the H₂/CO ratio 2 : 1; also, in the case of Fischer–Tropsch synthesis the ratio should be 3 : 1 [4].

The mechanism of the conversion reaction with the catalyst can be expressed as follows:





Notes: Z is the active site of catalyst surface, Z--C*H₂•, Z--CO, Z--O are chemisorptions of C*H₂•, CO and O are the first accepted stage for a limited process [5].

Natural gas conversion is the main industrial method of obtaining synthetic gas (syngas) for the production of ammonia, alcohol, acids, Fischer–Tropsch synthesis and other products. There are several ways for the above conversion: aerial, steam aerial, oxygenous, steam oxidation of hydrocarbons, etc.

The main process of obtaining syngas in the production of ammonia, methanol and synthesis of organic products is Steam Methane Reforming (SMR). The process has been carried out in a pipe oven with heating and a catalyst. The properties of the catalyst show the effect of the pipe oven and its lifetime on the productivity. SMR is most expensive among the present technologies as regards materials and energy. This research investigates the conversion of natural gas using the aerosol nanocatalysis (AnC) technology.

AnC is an effective direction in chemical technology as it allows obtaining superactive catalysts by permanent mechanical-chemical (mech-chem) activation

of the surface of catalyst particles *in situ*, which allows yielding nanoparticles from microparticles (powder of catalyst) after catalyst fragmentation by an inert material (glass or ferrous bullets).

A nanoparticle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Particles are further classified according to size: in terms of the diameter, fine particles cover a range between 100 and 2500 nanometers. On the other hand, ultrafine particles are sized between 1 and 100 nanometers [6].

In the AnC technology, the catalytic system consists of glass bullets ($d = 1.1 \text{ mm}$) (which represent an inert material) and catalyst powder (size about $5 \cdot 10^{-5} \text{ m}$). In the vibration process, the catalytic system's mixing and catalyst abrasion to the size of 10^{-7} – 10^{-9} m occur. The process of changing the catalytic system structure is illustrated in Figure 1. As shown in (Fig. 1, a), the catalytic system in the beginning (without mechanical action) is an inert material; catalyst microparticles, under the mechanical action, undergo fragmentation by the inert material to nanoparticles (Fig. 1, b). In the absence of mechanical action, after a certain time, the nanoparticles undergo agglomeration (Fig. 1, c) [7].

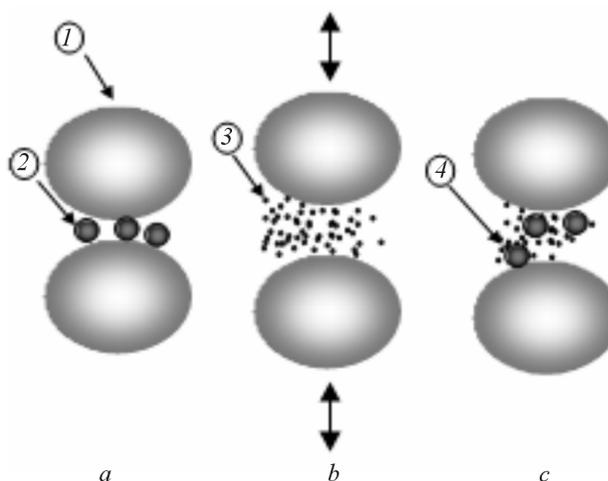


Fig. 1. The process of changing the catalytic system in AnC: 1 – inert material, 2 – catalyst microparticles, 3 – catalyst nanoparticles, 4 – agglomeration of catalyst particles

Experimental

The aim of the experimental research was conversion of natural gas by the AnC technology using a vibrating bed to get the most economical and technological effectiveness of syngas production.

A scheme of the experimental setup for investigating the AnC technology by a vibrated bed is shown in Figure 2.

The reactor (No. 3 in Figure 2) is a cylindrical apparatus; it works in the regime of mixing that can be provided mechanically. It performs a reflexive-progressive motion in the vertical plane in an electric furnace (2). The reactor has been designed to vibrate in

the diapason of 2–11 Hz. The reactor has branch pipes for inlet substances, outlet products of conversion, and a pouch for temperature measurement (11), which is linked to the control unit (1).

The catalytic system (particles of catalyst and inert material) is added to the reaction before start. Their motion provides mech-chem activation of the catalyst surface. Water feed can be done by a dosator (9) or an evaporator (10), or both. The mass of vapor in the evaporator could be measured by observing the change of evaporator mass before and after experiment. It could be also calculated by the rate of vapor when the period of the experiment is known, and the vessel which connects the reactor and the evaporator is as short as possible to avoid vapor condensation.

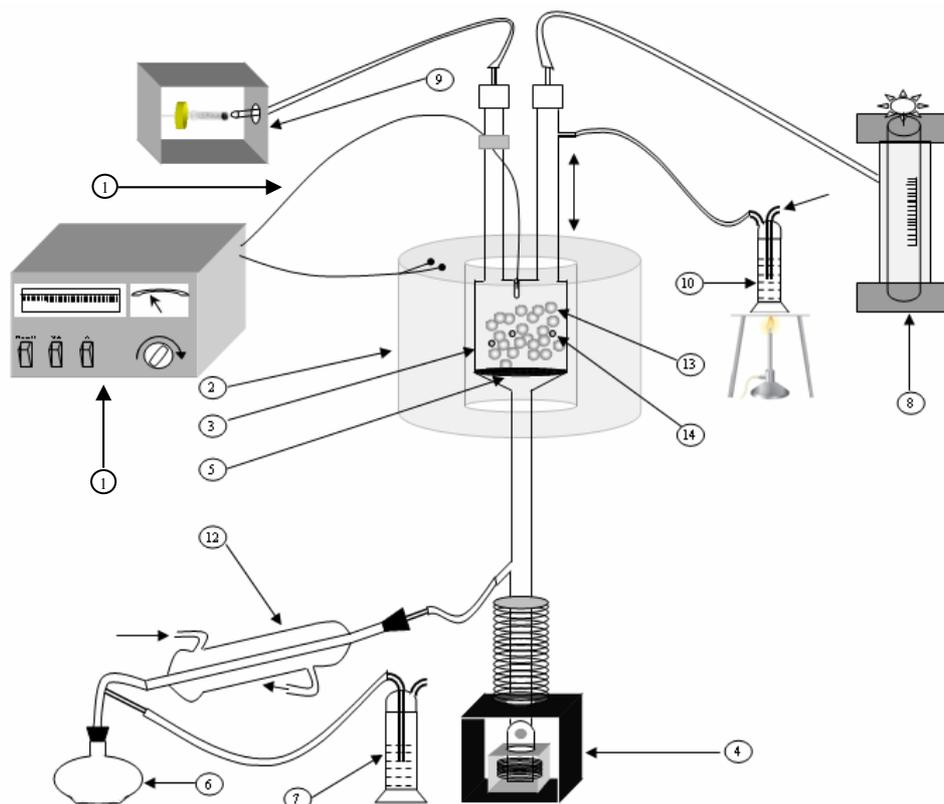


Fig. 2. Experimental setup of aerosol nanocatalysis by vibrating bed: 1 – control unit, 2 – electric furnace, 3 – reactor, 4 – vibration device, 5 – metallic filter, 6 – condensate receipt, 7 – cylindrical flask, 8 – rotameter of natural gas, 9 – water dosator, 10 – evaporator, 11 – thermocouple, 12 – condenser, 13 – dispersed material, 14 – catalyst

A particularity of this reactor is a filter (5) made from metal or a specific net in order to retain the particles of the catalyst and of the inert material. Thereby, the catalyst quantity remains unchanged.

By a permanent vibration of the catalyst, it is exposed to the mechanical effect of the inert vibrated material. It is dispersed, defects of its structure, appear, *i.e.* the properties of its surface, which determine its activity, are changed. In the reactor, 0.0001 gm of the catalyst is added, *i.e.* 2.38 gm/m³ of the reactor. Its easy to vary the quantity of the catalyst and to change the reactants. Currently, the technology of AnC allows obtaining syngas at a temperature interval of 600–800 °C and using the following types of catalysts: Fe₂O₃, K-902 D2 (8–10% NiO, 0.01% SO₃), GIAP-8 (Ni-Al₂O₃), Co₂O₃ and NiO at different conditions (for example, temperature change, vibration, content reactants).

METHOD OF EXPERIMENT. The duration of the experiment was determined according to the requirements of adequate products for analysis. The experiment could be divided into the following steps: 1. By Control unit (No. 1 in Figure 2), the electric furnace (2) could be switched on. 2. When the temperature reaches 300 °C, the vibration device (4) would be switched on, and the required frequency for the experiment (the intensity of mechanical-chemical activation) could be determined, 3.

Natural gas is allowed to flow through the vessel, and the water dosator is switched on at the same time with gas as soon as the temperature of the reactor reaches the level of the experiment (it could be determined also by the control unit). The products could be obtained from a cylindrical flask (7). With a pipette connected to a cylindrical flask, it was possible to take samples for analysis. 5. After the experiment is finished, the gas valve should be closed, the dosator is switched off, and the vibration device is switched off the last.

PREPARATION OF CATALYTIC SYSTEM. In the AnC technology, the catalytic system consists of dispersed material (glass bullets) (No. 13 in Figure 2) and catalyst powder (14); during the vibration process, there appear catalytic system's mixing and catalyst abrasion.

The feature of AnC is adsorption of catalyst quantity on the surface of dispersed material, and only the catalyst would be changed from microparticles to nanoparticles. Therefore, before starting the experiment, the dispersed material should be prepared as follows: (1) to prepare the dispersed material that could cover 50% of the reactor size and add it to the flask; 1.5 gm of the catalyst should be also added to the flask (2). The flask should be covered and mixed at a frequency no less than the required frequency of the experiment (3). This process should be applied for 20 min; then the mixture is taken to

separate the not adsorbed catalyst from the dispersed material covered by the adsorbed powder of the catalyst (4). After that, the dispersed material is carefully added to the reactor (5). Then it is necessary to add the same amount of the catalyst and repeat mixing at the same frequency, to separate the not adsorbed particles of the catalyst, and repeat this process until obtaining the same mass of dispersed material as before mixing.

After that, the dispersed material is added to the reactor. To keep the catalyst concentration without changing its amount, a metallic filter (see No. 5 in Figure 2) is located on the reactor outlet. Before the start, the leak-tightness of the reactor should be tested. After the experiment is finished, the catalytic system is withdrawn from the reactor and its state is checked (in case of the methane steam reforming reaction, carbon may be formed on the surface of the catalyst and dispersed material; if carbon hasn't formed, the dispersed material could be used for the next experiments).

ANALYSIS OF CONVERSION PRODUCTS. For the analysis of gas conversion, a chromatographer is used with a chromatographic column filled with zeolite 5A. Zeolite is ground to 0.2–0.4 mm and carefully washed with water, then dried at 80 °C for 2 hours, calcined in a muffle furnace at 400 °C for 4 hours, then cooled in a desiccator and put into the column. The column is located in the thermostat of the chromatographer, and for 2 hours at 100 °C the carrier gas is blown.

The analysis of gas conversion is carried out in two steps. In the beginning, in the first test CH₄, CO and CO₂ and in the second one hydrogen could be determined.

The analysis of conversion, which includes CH₄, CO and CO₂, is carried out with a chromatographer with a thermoconductivity detector and a device for temperature programming. Conditions of the chromatographic analysis are shown in Table 1.

Table 1. Conditions of chromatographic analysis to determine CH₄, CO and CO₂ in the process of steam methane reforming

Parameters	Value
Column, mm	1000
Diameter of column, mm	4
Temperature of thermostat, °C	50–180
Rate of temperature rise, °C/min	15
Detector current, mA	110
Rate of carrier gas (helium), ml/min	80
Rate of diagram tape movements, mm/min	10

The concentration of hydrogen in the gas conversion could be determined in the same column, but at the conditions that are shown in Table 2.

The other parameters of chromatographic analysis could be determined in the preliminary calibration of the chromatographer.

Table 2. Conditions of chromatographic analysis to determine hydrogen in the process of steam methane reforming

Parameters	Value
Temperature of thermostat, °C	50
Detector current, mA	110
Rate of carrier gas (nitrogen), ml/min	30
Rate of diagram tape movements, mm/min	10

METHODS OF RESULT PROCESSING. The time of keeping substances in the reactor:

$$\tau = \frac{V_{f.r.}}{V_{f.m.}} \cdot 3600 \text{ [s]},$$

where $V_{f.r.}$ is the reactor free volume, m³, and $V_{f.m.}$ is the rate of vapor–gas mixture, m³/h.

The free volume of the reactor could be determined depending on the whole volume of the reactor and the porosity of dispersed material ($\varepsilon = 0.6$):

$$V_{f.r.} = V_r - V_k \cdot \varepsilon,$$

where V_k is the volume of dispersed material added to the reactor, m³, and V_r is the volume of the reactor, m³.

Volume rate:

$$\psi = \frac{V_{f.m.}}{V_r}, \text{ year}^{-1}.$$

Catalyst concentration:

$$C_{cat} = \frac{m_{cat}}{V_{f.m.}} \cdot 1000 = \frac{m_{cat}}{V_r}, \text{ gm/m}^3 \text{ (volume of reactor)},$$

where C_{cat} is the catalyst concentration, and m_{cat} is the mass of catalyst, which has been added to reactor, gm.

Degree of methane conversion:

$$-X_C = \frac{(Vol_{CO} + Vol_{CO_2})_{prod.}}{\Sigma C_{vol_{prod}}} \cdot 100\%,$$

where X_C is the degree of methane conversion, Vol_{CO} is the volume percentage of CO (as product), Vol_{CO_2} is the volume percentage of CO₂ (as product), and $\Sigma C_{vol_{prod}}$ – is the summation of volume percentage products' that contain carbon, including CO and CO₂.

Results and discussion

The calculation of thermodynamics allows us to determine the conditions (temperature, pressure, reactant rate, ratio, etc.) of methane conversion that could be improved experimentally. The calculation has been done

using the САТРАПИС program. Figure 3 illustrates the theoretical relationship between the percentage of the gas components and temperature. As is shown, hydrogen yield increased with increasing the temperature. Therefore, for the Fischer–Tropsch process, the optimal variant

is increasing the temperature, and for ammonia production it is better to obtain the minimum quantity of CO during the maximum degree of methane conversion in which other oxidants (CO_2 or O_2) could be used.

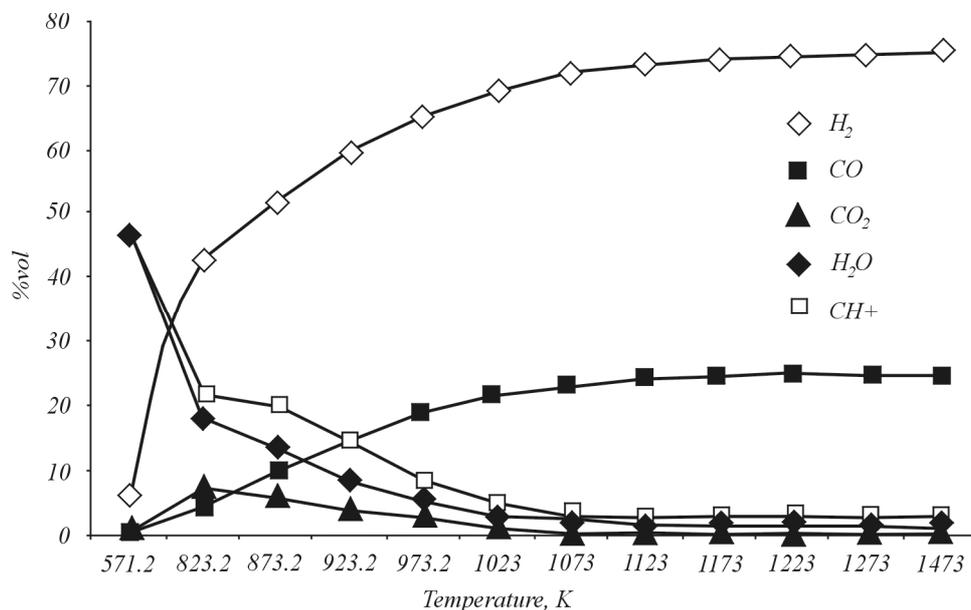


Fig. 3. Theoretical relationship between percentage of conversion product components and temperature

Figure 4 illustrates the change of products with changing the pressure. Methane conversion is decreased with increasing the pressure, but the rate of reaction and the productivity of the apparatus under pressure are

increased because of the decreased equilibrium constant. Therefore, pressure could be used to solve special industrial problems of syngas production.

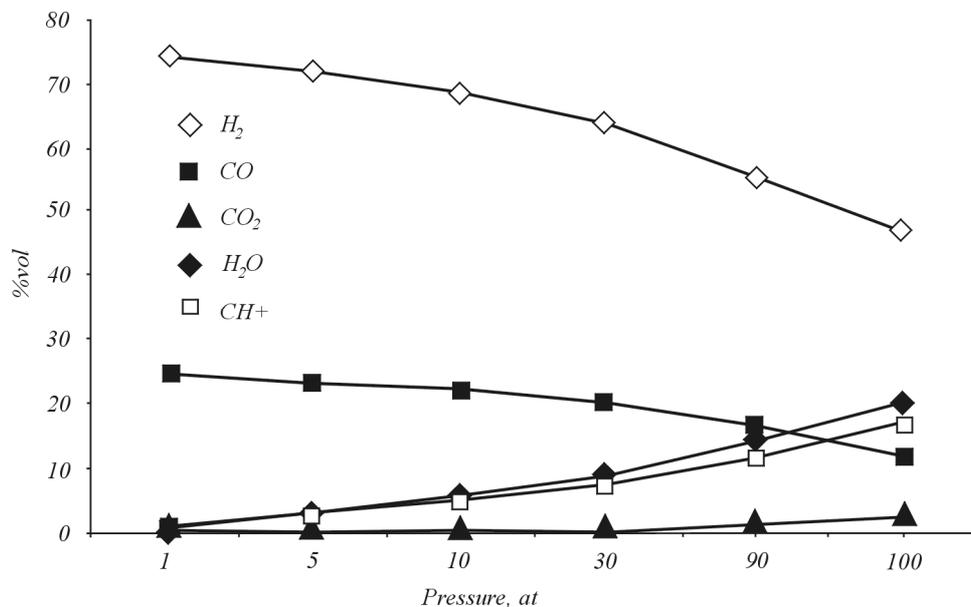


Fig. 4. Theoretical relationship between percentage of conversion substances and pressure

The $\text{H}_2\text{O} / \text{CH}_4$ ratio determines the production rate of syngas. Figure 5 shows that in case of ratio 1 : 1, the amount of hydrogen is 74.24%vol and 24.61%vol for

carbon monoxide. The figure shows that with increasing the $\text{H}_2\text{O} / \text{CH}_4$ ratio, the production of syngas would decrease.

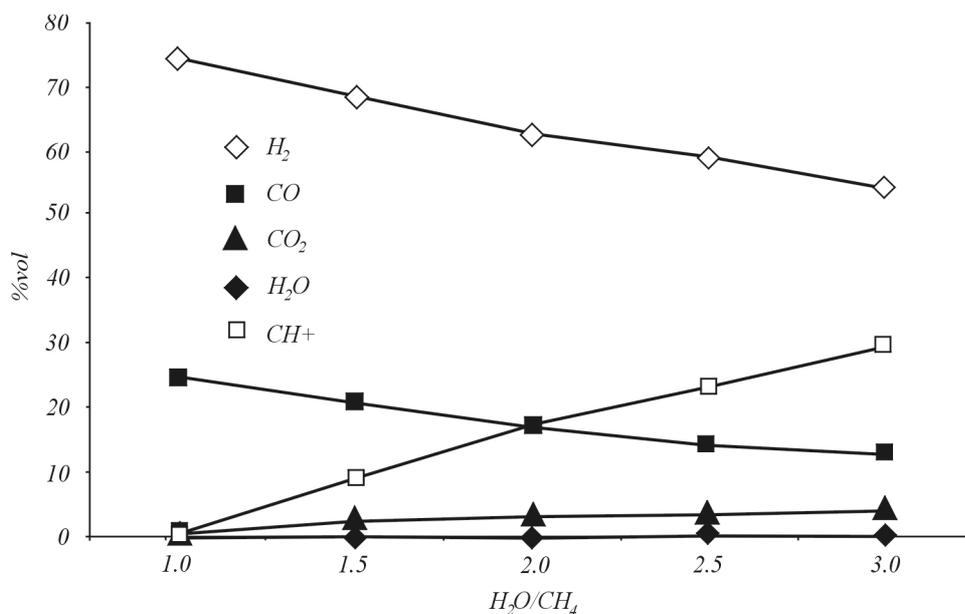


Fig. 5. Theoretical relationship between percentage of conversion products and H₂O / CH₄ ratio

Figure 6 illustrates the interrelation of the H₂ / CO ratio with temperature. The H₂ / CO ratio decreases from 8.99 to 3.5 at 700 °C (973.15 K), and with increasing the

temperature the ratio remains approximately at the same level of 3.0–3.5, *i.e.* over 700 °C the H₂ / CO ratio would not depend on increasing the temperature.

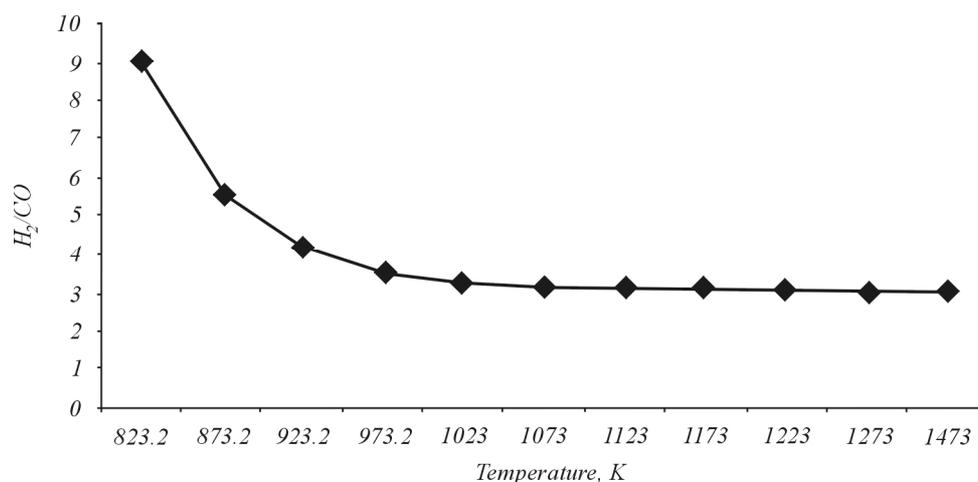


Fig. 6. Theoretical relationship between H₂ / CO and temperature

During the experimental work of the aerosol nanocatalysis reactor (volume 42 m³), changing the following parameters underwent changing:

- temperature 550–700 °C;
- frequency of mech-chem activation 2–5 Hz;
- molar ratio vapor/gas in the inlet mixture 1 : 1–6.5 : 1;
- contact time 1–10 s.

The activity of the catalysts such as Fe₂O₃, K-905D2 (8–10% NiO, 0.01% SO₃); GIAP-8 (Ni-Al₂O₃), Co₂O₃ was checked; their concentration in the experiment was 2.38 gm/m³ of the reaction volume.

The experimental data on the nickel catalyst and its comparison with the maximum possibility (equilibrium) of gas contents are illustrated in Table 3.

Data in Table 3 allow to calculate the contact time required to reach the equilibrium composition of gas conversion.

The obtained data had to be compared with data obtained without a catalyst. As is known [8], the rate of methane interaction with vapor without a catalyst is too low. Thus, by heating the mixture (CH₄ : H₂O = 1 : 2–1 : 3) in a quartz reactor at static conditions (contact time 3 hours), the level of methane conversion at 700 °C is 3%.

In the conditions of AnC (Table 3), the level of methane conversion at 700 °C and at the contact time 9.2 s is 11.47%; *i.e.* 4488 times greater than the thermodynamic process; thus, the experiment has shown an explicit catalytic activity of NiO using no more than 2.38 gm/m³ of the reactor for the process of steam reforming via AnC.

Table 3. Results of experimental research and comparison of conversion gas in the equilibrium case (cat NiO, $V_{\text{bullet}} = 20 \text{ cm}^3$, $m_{\text{cat}} = 0.0001 \text{ gm}$, $C_{\text{cat}} = 2.38 \text{ gm/m}^3$)

$T, \text{ }^\circ\text{C}$	Volume rate, l/h		$\text{H}_2\text{O} / \text{CH}_4, \text{ mol}$	$\tau, \text{ s}$	Products in outlet, %vol				$\text{H}_2 / \text{CO}, \text{ mol}$	$\alpha\text{C}, \%$	
	CH_4	Vapour			H_2	CO	CO_2	CH_4			
600	1.17	14.3	4.1	6.3	19.98	3.09	25.47	18.47	6.5	61.7	
Equilibrium composition of products, %vol					32	1.6	6.8	7.9	20	51.5	
650	1.1	15.2	4.4	6.0	10.53	2.7	6.8	77.16	3.9	11.0	
650	1.1	15.2	4.4	6.0	10.74	6.75	2.1	80.04	1.6	9.9	
Equilibrium composition of products, %vol					36.9	2.8	7.2	4.9	13.2	67.1	
700	1.14	9.3	2.5	8.5	1.7	0.51	0	25.54	3.3	1.96	
	Equilibrium composition of products, %vol					49.9	7.4	6.9	6.1	6.7	70.0
	1	9.3	2.7	8.8	21.73	1.54	3.4	59.4	14.1	7.7	
Equilibrium composition of products, %vol					48.9	6.9	7.0	5.5	7.1	71.6	

τ – residence time; αC – degree of carbon conversion.

Data on catalytic conversion process over heterogeneous catalysts within the temperature interval 600–700 °C in available resources is absent. It is clear that a heterogeneous catalyst is not effective at these relatively

low temperatures. Therefore, a comparison of experimental data was performed with a heterogeneous catalyst at higher temperatures (See Table 4).

Table 4. Comparison of thermal and heterogeneous catalytic processes and aerosol nanocatalysis for steam reforming of natural gas

Parameters	Process		
	Thermal	Heterogeneous catalyst	AnC
$T, \text{ }^\circ\text{C}$	1350–1400	850	650
$P, \text{ MPa}$	2–3	1.5–3.0	2
$\text{H}_2\text{O} : \text{CH}_4$	~2.6	3.7	2.5
$E_A, \text{ KJ/mol}$	–	272	130
Rate constant k	$0.14 \cdot 10^{-4}$	1105.6	1696.6
$\Delta x / \tau$	$3.4 \cdot 10^{-4}$	–	1.245
Catalyst	–	$\text{NiO}/\text{Al}_2\text{O}_3$	NiO (AnCVB)
Apparatus	In this interval of temperatures the process is not implemented in the industry	Pipe oven	Reactor AnC
$V_r, \text{ m}^3$		55	40.5
$V_{\text{cat}}, \text{ m}^3$		55	$6.4 \cdot 10^{-5}$
$m_{\text{Kat}}, \text{ kg}$		82500	0.0964
Performance of catalyst, $\frac{Kg_{\text{raw}}}{Kg_{\text{cat}} / \text{year}}$		0.22	3455988.3
Reactor performance $\frac{V_{\text{raw}}}{V_{\text{reactor}}}$		1363,6	3938.02

According to the research, AnC has the following advantages for methane steam reforming: it *decreases* the temperature of the process (to 200 °C), the flow rate of steam, the quantity of a catalyst (about 10^{-5} times), the volume of the reactor (about 1.5 times), and *increases* the rate of chemical conversion (4488 times as compared with the thermal process and about 1.7 times as compared with the heterogeneous catalyst), the performance of the

catalyst 1.5 million times, and the performance of the reactor 3 times).

Conclusions

The possibility of using the aerosol nanocatalysis technology has been proven to obtain syngas and in the field of methane conversion (Steam Methane Reforming)

with a vibrating bed, so it is possible to use AnC, and it would be effective at $T = 650\text{--}700\text{ }^{\circ}\text{C}$.

The experimental setup is very flexible to change from one condition to another. By using different parameters it is possible to obtain different ratios of products. Besides, the experimental setup has advantages in kinetic investigations and shows the flexibility of the parameters. The rate of the process in case of AnC is 4488 times greater than the thermal one and 1.7 times greater than the heterogeneous catalyst, and requires lower temperatures (less than $200\text{ }^{\circ}\text{C}$).

The influence of mech-chem activation allows to reduce the amount of the catalyst and induce the selectivity. The volume of an AnC reactor is 1.5 times less than of the reactor in a pipe oven with a heterogeneous catalyst, and the active catalyst in the AnC is NiO.

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КОНВЕРСИЯ ПРИРОДНОГО ГАЗА В ПРОЦЕССЕ ПАРОВОГО РИФОРМИНГА С ПОМОЩЬЮ АЭРОЗОЛЬНОГО НАНОКАТАЛИЗА

Р э з ю м е

В статье рассматривается возможность проведения паровой конверсии метана с целью получения смеси оксидов углерода и водорода с использованием технологии аэрозольного нанокатализа AnC. Сущность метода AnC состоит в генерировании наночастичек катализатора с размерами 8–100 нм и их постоянной механохимической активации непосредственно в реакторе во время проведения процесса конверсии. Представлены описание лабораторной установки и методики постановки оригинального эксперимента. Исследовано поведение ряда возможных катализаторов (Fe₂O₃, K-902 D2, GIAP-8, Co₂O₃ и NiO). На основании полученных экспериментальных данных доказано, что лучшие каталитические свойства показал NiO. При этом катализ в условиях AnC возможен и эффективен для процесса паровой конверсии метана при температуре 650–700 °С. Обработка результатов эксперимента показала, что скорость процесса в AnC в 3500 раз выше, чем в термическом, и в 1,7 раза выше, чем в гетерогенном катализе при одновременном уменьшении температуры на 200 °С.