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Plasmachemical synthesis and regeneration (activation) of nanostructured catalysts for steam conversion of methane

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Abstract

Under the conditions of thermal electric-arc plasma in a plasmachemical reactor (PCR) with ‘‘cold’’ (CW) and ‘‘warm’’ (WW) walls, catalysts were synthesized and/or regenerated to be used for conversion of methane with steam. The ‘‘plasma’’ samples thus produced were characterized by means of electron microscopy, X-ray diffraction, and chemical analyses.

It was established that the plasma samples are reduced 2–4 times as fast as their conventional analog G56A. Upon application of an external high-frequency (HF) discharge, the reduction rate of the plasmachemically synthesized samples rose by about 10%. The catalysts synthesized in a CW PCR had lower activity than their industrial analog G56A, while those synthesized in a WW PCR had activity comparable to that used in the industry (HIMKO Company, Vratsa, Bulgaria); moreover, under certain technological conditions, they were more active (by up to 10%), e.g., in the case of heterogeneous catalytic interaction between methane and water steam with applied HF discharge.

Keywords: Plasmachemical synthesis; Regeneration; Activation; Nanostructured catalysts; Steam conversion of CH_4

1. Introduction

The theory and practice of the heterogeneous catalysis have proved that the activity of solid-state phase catalysts is determined by their chemical and phase content, their crystal structure and the value of their active specific surface. Usually, the active and total specific surfaces dependence on the temperature have similar slopes. On the other hand, the thermal plasma (TP) conditions lead to the production of compounds with highly developed specific surface and particle size in the order of a few tens of nanometers, which usually exhibit high catalytic activity [1–6]. When the processes of plasmachemical synthesis (PCS) of nanodispersed powders (NDP) are connected with certain chemical reactions, and when an efficient quenching of the reaction products takes place, conditions are created for condensation of the NDP with a specific distribution of the additive components and with large number of crystal lattice defects, so that the NDP exhibit high catalytic activity in the heterogeneous catalytic processes. Thus, in certain cases, the plasmachemical technique (PCT) proves to be efficient in the synthesis of highly active catalysts.

Analyzing and summarizing the experimental data accumulated, the studies on PCS and activation of catalysts, one can identify three main trends [7–10]: (1) PCS and activation of catalysts in condensed phase; (2) plasma-assisted deposition of catalytically active compounds and compositions on carriers; (3) activation of the heterogeneous catalytic processes in the conditions of different plasma discharges.

The process of steam conversion of methane (natural gas reforming) is a basic one in the production of hydrogen and, hence, of ammonia, nitric acid, ammonium nitrate and/or urea. It forms the basis of the catalytic cleaning of greenhouse gases of methane. The following two independent reactions take place during the steam conversion of CH_4:

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 206\,\text{kJ} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + 41\,\text{kJ} \tag{2}$$

The overall reaction can be written as

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 - 165\,\text{kJ} \tag{3}$$

The large specific surface and high dispersity of the catalysts, the defects in the crystal structure, the phase

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content and the homogeneous distribution of the catalytically active components among the promoters (and vice versa) determine the high catalytic activity of the "plasma" catalysts. The fact that, following the technique considered, the catalysts are synthesized at high temperatures and are separated as a condensed phase, bring about their increased thermal stability and duration of highly efficient use. The ingredients' homogeneous distribution on the "plasma" catalysts composition contributes to the decrease of their sensitivity to poisons, while the possibility to fix strictly the composition warrants their selectivity. The large specific surface of the nano-dispersed "plasma" catalysts (NDPC) and the large number of defects in the crystal lattice assist in the fast reduction of the catalysts. By means of pressing or by deposition on carriers, one can achieve high mechanical strength of the catalysts.

Accounting for the basic advantages of the plasmachemical processes (PCP), namely [1–4] one-stage production process, high temperatures and high rates, possibility for miniaturization of the equipment, simplicity of the modeling, optimization and control, standardization of the technological facilities and organization, etc., one can assert that the PCT for preparation of catalysts will soon prove its indisputable advantages. One should also bear in mind that the relative share of the catalysts' costs on the overall value of the industrial ammonia production is small (within 2–3%) and, therefore, the catalysts' price is not a critical factor.

The present paper presents our results from the PCS or regeneration in electric-arc thermal plasma, and the activation in HF discharge during the heterogeneous catalytic interaction, of catalysts for steam conversion of methane, and to compare their reducibility and catalytic activity.

2. Experimental

Our long-term studies, aimed at producing catalysts as condensed-phase products, have been carried out in equilibrium (quasi-equilibrium) or non-equilibrium plasma conditions. As raw materials, we have used the compounds that make up the catalysts, i.e., the plasma only disperses and activates the catalysts compositions; the other technique applied was to synthesize the catalysts during the PCP [1–6].

Our previous studies related to the synthesis and/or regeneration of nickel catalysts for steam conversion of methane have been discussed in detail in specialized scientific publications [1–8,11–29].

The analysis of the thermodynamic calculations for four compositions of the Ni–Al–O–Ca–Mg system, namely I variant: Ni – 2.0002 mol kg^{-1} (11.74 mass%); Al – 14.722 mol kg^{-1} (39.72 mass%); O – 26.023 mol kg^{-1} (41.64 mass%); Ca – 1.4202 mol kg^{-1} (5.69 mass%) and Mg – 0.50004 mol kg^{-1} (1.21 mass%); II variant: Ni – 0.42135 mol kg^{-1} (2.47 mass%); Al – 3.1012 mol kg^{-1} (8.37 mass%); O – 54.819 mol kg^{-1} (87.71 mass%); Ca – 0.29917 mol kg^{-1} (1.20 mass%) and Mg – 0.10534 mol kg^{-1} (0.25 mass%); III variant: Ni – 0.42135 mol kg^{-1} (2.47 mass%); Al – 3.1012 mol kg^{-1} (8.37 mass%); O – 54.819 mol kg^{-1} (87.71 mass%); Ca – 0.29917 mol kg^{-1} (1.20 mass%) and Mg – 0.10534 mol kg^{-1} (0.25 mass%); IV variant: Ni – 0.047378 mol kg^{-1} (0.28 mass%); Al – 0.34871 mol kg^{-1} (0.94 mass%); O – 61.64 mol kg^{-1} (98.62 mass%); Ca – 0.03364 mol kg^{-1} (0.13 mass%) and Mg – 0.01844 mol kg^{-1} (0.04 mass%) showed [3,4,20,29] that in the higher end (above 3100 K) of the 1000–3700 K temperature interval, the gas-phase of the system contains predominantly NiO, AlO and CaO. The condensed phase of the equilibrium content should comprise $CaO{\cdot}2Al_2O_3$ up to 3200–3700 K, Al_2O_3 also up to 3200–3700 K, NiO up to 2500–3000 K, depending on the molar (mass) ratio of the initial system components Ni–Al–O–Ca–Mg. We have also performed thermodynamic calculations for temperatures exceeding 6000 K, where all components are in gas phase as radicals, molecules of the respective elements, ions and electrons. Regrettably, our calculations did not account for the thermodynamic probability for condensation of a phase of the spinel-type $NiAl_2O_4$ ($NiO{\cdot}Al_2O_3$), which was experimentally observed also in the synthesis and regeneration of catalysts samples, and was confirmed by X-ray analysis.

Making use of the plasmachemical installation, whose schematic diagram is shown in our earlier publications [3,4,17,18,20], we synthesized samples of catalysts for steam conversion of methane with the following ingredients content:

1. PCS of AN-type samples via oxidation of Ni and Al at a mass ratio of Ni:Al = 1:1.5 at a temperature in the PCR of 3200–3300 K, and flow rate of the plasma-forming gas (Ar) 0.79 g s^{-1} and of the oxidizing (powder-carrying gas – O_2) 0.29 g s^{-1}.
2. PCS of PC-type catalytic compositions for natural gas reforming from raw material with content (mass%): Al_2O_3 – 73; NiO – 15; CaO – 8 and Mg – 0.2 in the temperature interval 1000–4000 K at flow rate of the plasma-forming gas (Ar) 0.79, 1.19 and 1.59 g s^{-1} in a CW PCR. Treatment of spent or deactivated G 56A and G 56H catalysts in electric-arc low-temperature plasma (LTP) in the 1000–5000 K temperature interval at flow rate of the plasma-forming gas (Ar) of 0.9 g s^{-1}, of powder-carrying gas (Ar) of 0.32 g s^{-1} or (O_2) 0.29 g s^{-1} in a CW or WW reactor.

The consumption rate of the powder material was 2–3 g min^{-1}, depending on the amount of powder-carrying gas in the vibration powder-feeding device and on the revolutions per minute of the piston vibration powder-feeding device. The installation's output was within the 100–150 g h^{-1} range.

3. Results and discussion

The syntheses carried out resulted in the production of catalyst samples with content (mass%): NiO – 9–15; Al_2O_3 – 73–89; CaO – 0.7–8; MgO – 0.2–0.8, as well as NiO – 15; Al_2O_3 – 85. The following initial batches were used: Ni:Al = 1:5.5 and Mg, as well as NiO, Al_2O_3, CaO and MgO.

The catalyst samples were characterized by their specific surface, bulk weight, chemical composition using emission spectral, derivatographic, X-ray diffraction, electron microscopy, etc. analyses. Some parameters of plasmachemically synthesized samples and of industrial catalysts are presented in Table 1.

In these studies, the temperature in the PCR was varied from 2900 to 3600 K (Table 2), with the NiO content varying in the 5.5–14.3 mass% range.

The plasma-forming gas was Ar at a flow rate of 1.19 g s^{-1}, while the powder-carrying and oxidizing gas was O_2 at a flow rate of 0.29 g s^{-1}. In all experiments, the current was kept constant (400 A), with the discharge voltage being varied in a narrow range (23.5–26 V) via varying the anode–cathode distance by means of the plasmatron's adjusting ring. The specific surface was within the 110–120 m^2 g^{-1} limits, while the bulk weight changed between 130 and 140 kg m^{-3}.

The X-ray diffraction analysis revealed that the NDP of the product contain the oxides of the added elements – NiO and α-Al_2O_3 (Fig. 1).

According to the electron microscopy analysis (Fig. 2), the shape of the particles obtained was close to the spherical, while their size fell within the 10–30 nm range.

Table 3 shows the dependence of the change of the degree of reduction of a fresh industrial catalyst (G 56A), of sample No. 5 (Table 2), and of the same sample after carrying out a reduction process in HF discharge (power 400 W and frequency 13.56 MHz) as a function of the reduction process duration. Fig. 3 shows the same dependence of sample No 6 (Table 2). The catalyst samples reduction was performed with 1 cm^3 of catalyst at a volume rate of the reducing agent (technical grade H_2) of 20 000 h^{-1}. The studies on the reduction dynamic and kinetics were carried out on the flow installation shown schematically in Fig. 4. The results in Table 3 and Fig. 3 demonstrate that the main amount of water is released during the first hours of the reduction process. This is due to the fact that the reducing agent (H_2) first interacts with the particles' surface layer, with the rate of the process at lower temperatures (up to 673 K) being

Table 1
Some technological parameters of the synthesis process and some physical–chemical characteristics of "plasma" and of standard catalysts for steam conversion of methane[a]

No. and type of catalyst	T_{av}[b] (K)	Ar_{pl}[c] (g s^{-1})	Sample composition (mass%)				Bulk weight kg m^{-3}	S (m^2 g^{-1})
			NiO	CaO	MgO	Al_2O_3		
1. AN	3200	0.79	12.7	–	–	78.3	130	108
2. PC	2800	0.79	8.5	0.7	0.4	88.9	470	58
3. PC	3500	1.59	12.8	1.3	0.2	85.7	490	19
4. $G56A_{act}$	3000	0.79	8.8	0.7	0.6	89.9	490	13
5. $G56A_{act}$	900	0.79	12.5	1.0	0.3	86.2	700	7
6. $G56A_{act}$	1400	0.79	12.9	1.2	0.3	85.6	440	12
7. G56A	–	–	15.0	8.0	0.2	76.8	800	4
8. G56H	–	–	15.0	8.0	0.2	76.8	750	4
9. Spent	–	–	9.4	0.9	0.8	88.9	900	3.6

[a] The studies are carried out in a CW reactor (sample No.4 in a WW PCR); flow rate of powder-carrying gas (oxygen) 0.29 g s^{-1} (for sample No. 6 – argon – 0.32 g s^{-1}).
[b] T_{av} – mass-averaged temperature in the PCR.
[c] Ar_{pl} – flow rate of the plasma-forming gas – argon.

Table 2
Some technological parameters and properties of the product in the plasmachemical study of the Ni–O–AI system for flow rate of the plasma-forming argon 1.19 g s^{-1} and of powder-carrying gas oxygen 0.29 g s^{-1}

No.	IA	UV	WkW	T_{av}[a] (K)	H_{av}[b] (kJ kg^{-1})	T_{av}[c] (K)	NiO (mass%)	Al_2O_3 (mass%)	ρ (kg m^{-3})	S (m^2 g^{-1})
1	400	26	10.4	6350	3310	3610	14.3	78.9	130	122
2	400	26	10.4	6210	3220	3470	5.5	85.6	110	107
3	400	26	10.4	6220	3220	3480	6.0	84.9	140	117
4	400	25.5	10.2	5400	2800	3100	13.7	80.1	140	119
5	400	25.5	10.2	5400	2800	3200	12.7	78.3	130	108
6	400	25	10.0	4860	2540	3020	7.3	82.4	140	115
7	400	23.5	9.4	4220	2240	2880	7.9	86.2	130	119

[a] T_{av} – mass-averaged plasma temperature.
[b] H_{av} – mass-averaged plasma enthalpy.
[c] T_{av} – mass-averaged temperature in the PCR.

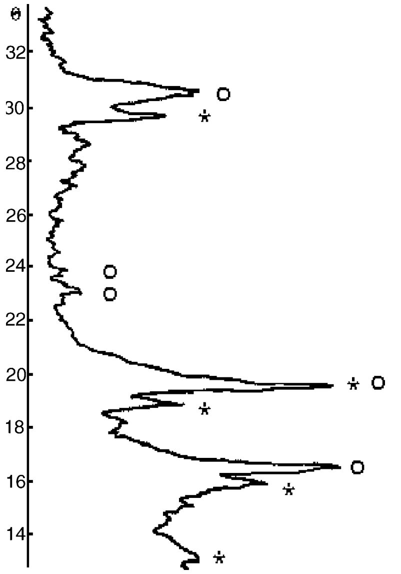

Fig. 1. X-ray diffraction pattern of sample No. 3, Table 2: (*) NiO; (○) Al_2O_3.

Table 3
Change of the degree of reduction of a fresh industrial catalyst type G 56A,of sample No. 5 in Table 2 and of the same sample in HF discharge with power 400 W as a function of the time in isothermal reduction mode at 773 K

No.	Time, τ (h)	Reduction degree B (%)		
		Fresh G56A	Sample No. 5, Table 2	
			Without Hf discharge	With Hf discharge (400 W)
1	0.5	2.2	21.5	23.6
2	1.0	3.3	69.8	66.8
3	1.5	6.2	75.0	82.5
4	2.0	10.0	83.6	91.6
5	2.5	16.0	87.1	95.8
6	3.0	20.0	94.0	98.1
7	3.5	21.4	96.6	100.0
8	4.0	25.0	99.1	100.0
9	4.5	25.7	100.0	100.0
10	5.0	26.8	100.0	100.0
11	5.5	27.6	100.0	100.0

limited by the rate of chemical interaction of H_2 with NiO, i.e., the process takes place in the kinetic region. As the process progresses in the depth of the catalyst particles (sample G 56A), its rate decreases due to the reverse diffusion of water vapor from the particles' interior to their surface being hindered. As one can see, the sample synthesized in LTP is completely reduced within 4 h, while the G 56A sample reaches 25% reduction for the same period of time under the same conditions. When the process is carried out in HF discharge, the degree of reduction of the plasmachemically synthesized sample exceeds by about 10% that of the same sample processed without such a discharge.

During the induction period of the reduction process, which comprises the time period for increasing the temperature from 473 to 773 K, a new phase of elemental Ni starts being formed, which catalyses the natural gas reforming. In the second period (the autocatalytic one), nuclei of the new phase of elemental Ni have already been formed; thus, the reduction process is significantly eased and its rate grows with the time, together with the growth of the boundary surface between the two phases (NiO and Al_2O_3). At the end of the process – the period of de-reduction – the amount of moisture released drops to zero, indicating the end of the process. It is possible that at the end of the reduction (B = 90% and more), concentrated solid solutions of the promoters (CaO, MgO, Al_2O_3) remain, so that the further reduction of the catalyst to 100% degree runs with considerable difficulty.

The experimental results show (Table 3) that the rate of reduction of NDPC containing 12.7% of NiO and 78.3% of Al_2O_3 is three times as high as that of the industrial catalyst

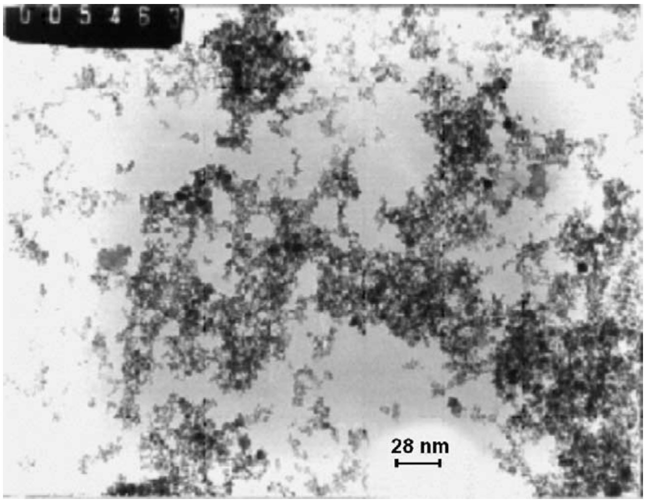

Fig. 2. Electron microscope photograph of sample No. 1, Table 3; magnification: 36 000, 10 mm = 28 nm.

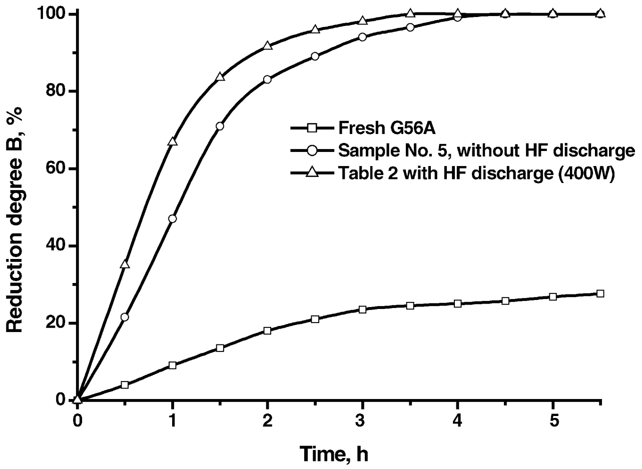

Fig. 3. Reduction degree B (%) of samples as a function of time (h). (□) fresh G56A; (○) sample No. 6, Table 2, without HF discharge; (△) sample No. 6, Table 2, with HF discharge (400 W).

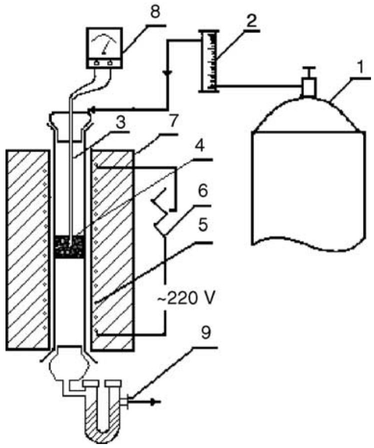

Fig. 4. Schematic diagram of a flow installation for dynamic and kinetic studies of reduction processes: 1 – hydrogen bottle; 2 – flow-rate meter; 3 – quartz reactor vessel; 4 – catalyst; 5 – electric furnace; 6 – auto-transformer; 7 – thermocouple; 8 – milivoltmeter; 9 – U-shaped tube filled with fused KOH.

type G 56A; we believe that this is due to the following: (1) The sample obtained in LTP has specific surface of 108 $m^2 g^{-1}$, while that of the G 56A catalysts is 4 $m^2 g^{-1}$. The highly developed surface allows intensive transport of hydrogen molecules to the pores of the sample being reduced, so that the overall reduction process is intensified (at diffusion control). (2) The presence of promoters in the industrial catalysts slows down the process of NiO reduction due to the blockage of the transport capillaries in the latter.

Under the isothermal reduction mode at 773 K adopted, the process runs most intensively during the second and third hours. At lower temperatures, the reduction takes place at a very uneven rate, with the amount of water released for unit time varying in a wide interval, which points to the complex reduction mechanism and kinetics. Carrying out the isothermal reduction at 773 K leads to a more uniform course of the reduction process.

We further performed studies on the process of reduction of the plasmachemically synthesized catalysts for steam conversion of methane in the conditions of an applied external HF field. The HF source was a Fisiotherm-type HF generator creating a HF electromagnetic field with frequency 13.56 MHz and four different output powers: 15 ± 2.55, 40 ± 6, 310 ± 46.5 and 400 ± 60 W. The operating pressure in the system was kept at about 7×10^2 Pa (due to the relatively low HF power generated – up to 400 W). At this, and lower pressures, and at CH_4 flow rate of 20 $dm^3 h^{-1}$, the gas discharge was stable and was not quenched by the catalyst introduced in the reactor. Within the range of HF powers quoted and pressures up to 7×10^2 Pa, the electron temperature in the catalytic reactor had values of $(10–25) \times 10^3$ K, while the temperature of the heavy particles (atoms, molecules and ions) did not exceed 800 K [1]. Thus, the topochemical process of reduction of NiO in the plasmachemically synthesized catalysts took place under the influence of the high hydrogen temperature (773 K) on the one hand, and of the high electron temperature of the HF discharge, on the other.

At a pressure of 7×10^2 Pa, the experimentally established hydrogen flow rate was 20 $dm^3 h^{-1}$, and a stable discharge could only be created at HF generator output powers of 220, 310 and 400 W; this is why our experiments were only performed at these three values of the HF power.

Moreover, in the course of the experiments, we had to seek an optimal inductor configuration, in view of forming a homogeneous HF discharge. Thus, we experimented with electrodes of different shape – ring-like, spiral and in the form of stripes. In the former two cases, we observed successive dark and light sections in the plasma space, with the light sections being formed in the plane of the rings or in the windings of the spiral, and the dark sections, in the distance between them. Because of the inhomogeneity of the plasma column, these inductors were not used in the further experiments. The most homogeneous HF discharge was achieved by using an inductor formed by two copper strips with length of 500 mm placed in parallel to the quartz reactor. The plasma column then was uniformly light and stable along the entire reactor length.

One can see that for 5 h since the process onset the industrial catalyst reaches a reduction degree of about 27%, while the plasmachemically synthesized samples are fully reduced. This is most probably due to the fact that the plasmachemical samples have much better developed specific surface (higher dispersity) compared to the industrial catalyst; moreover, the quenching conditions of the reaction products in the CW PCR result in the fixing of the newly formed phases, i.e., in the freezing of quasi-equilibrium compositions, which, in all probability, eases the process of interaction of H_2 with the oxygen in NiO.

Fig. 5 presents the dynamics of reduction of some catalyst samples, as compared with that of the conventional catalyst G 56A. In order to be able to juxtapose the results of the dynamic and kinetic studies, using a press we produced pellets at a pressure of 4000 kg cm^{-2}, which, after being

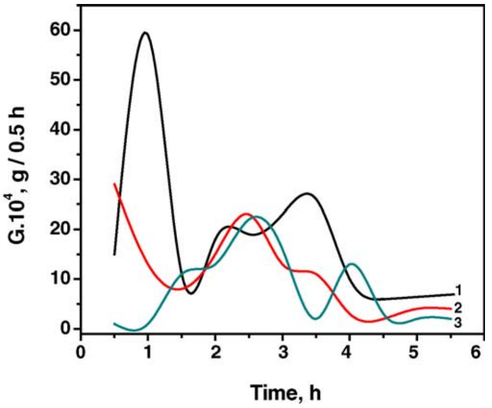

Fig. 5. Reduction dynamics of catalysts samples: 1 – sample No. 3, Table 2; 2 – sample No. 3, Table 1; 3 – catalyst G 56A.

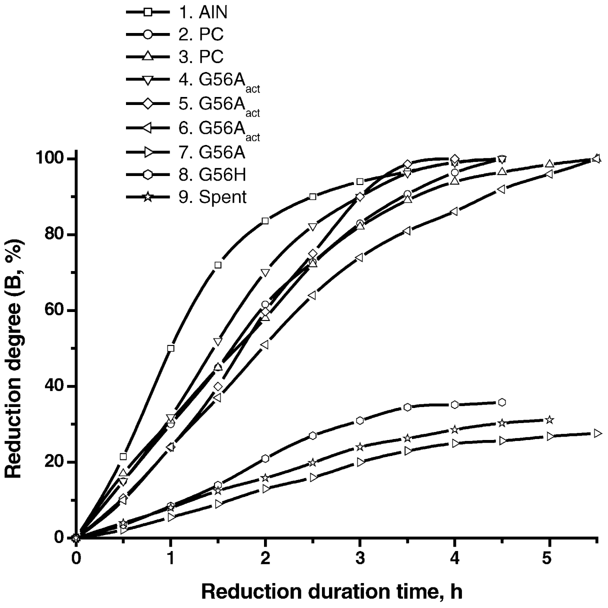

Fig. 6. Reduction degree B (%) of samples (N and type of samples are the same as in Table 1) as a function of time (h).

milled and fractioned were reduced isothermally at 773 K in the quartz flow installation shown schematically in Fig. 4.

Summarizing the results of the studies on the PCS of nano-dispersed catalysts for natural gas reforming in a CW PCR, we should note that the plasmachemically obtained samples are reduced 2–4 times as fast as the currently industrial catalysts of the types G 56A and G 56H; moreover, when an external HF field is applied, the reduction rate increases by an additional 10%.

Fig. 6 shows the reduction degree of the samples (described in Table 1) as a function of time.

The studies on the samples' activity were performed on a flow installation for natural gas reforming at a pressure of 0.1 MPa [3,4,20], volume flow rate of the dry natural gas of 2000, 5000, 7500, 10 000 and 20 000 h^{-1} in the temperature interval 873–1073 K and at a steam:gas ratio of 2:1, corresponding to a temperature in the gas-steam saturator of 360 K. During the steam conversion of CH_4, the two independent reactions ((1) and (2)), or the overall reaction (3), take place.

The gas analysis of the converted steam–gas mixture was performed by using an Orsa gas analyzer, with the content of CO_2, CO and O_2 being determined, and the H_2 content being calculated by taking into account the reactions quoted above. The remainder to 100% is assumed as being unreacted CH_4.

The process of natural gas reforming is characterized by the basic parameter of degree of CH_4 conversion:

$$\eta\,(\%) = \frac{V_{CH_4}^{in} - V_{CH_4}^{out}}{V_{CH_4}^{in}} \times 100 \qquad (4)$$

where $V_{CH_4}^{in}$ is the CH_4 volume at the converter's input at normal conditions in m^3 and $V_{CH_4}^{out}$ the CH_4 volume at the converter's output at normal conditions in m^3. The catalyst's efficiency is

$$G = \frac{V(H_2 + CO)}{V_{cat}}, \frac{m^3(H_2 + CO)}{m^3_{cat}} \qquad (5)$$

where $V(H_2 + CO)$ is the volume of the amount $H_2 + CO$ obtained under normal conditions in m^3 and V_{cat} the catalyst volume in m^3.

The catalyst's efficiency is expressed by the ratio between the practical degree of CH_4 conversion and the equilibrium degree of conversion:

$$\eta_{eff} = \frac{\eta}{\eta_{eq}} \qquad (6)$$

where η is the experimentally determined degree of conversion in % and η_{eq} the equilibrium degree of conversion (%).

The studies on the activity of the standard G 56A catalyst, of a plasmachemically regenerated sample, of a plasmachemically synthesized sample and of a plasmachemically synthesized sample subsequently activated in a HF discharge are summarized in Table 4 and Fig. 7. The analysis of the results of the studies on the samples' catalytic activity demonstrates that the activity of an NDPC regenerated in thermal electric-arc plasma (II) is lower than that of the conventional G 56A catalyst (I); the activity of NDPC synthesized of thermal electric-arc plasma (III) is comparable to that of (I); while the activity (efficiency) of the sample synthesized in thermal electric-arc plasma and activated in HF discharge (IV) is higher than that of (I) by about 10%.

Table 4
Activity at volume rate 2000 h^{-1} and temperature 923 K of standard catalyst for steam conversion of methane G 56A (I), plasmachemically regenerated spent catalyst (II), catalysts synthesized in electric-arc thermal plasma (III) and catalyst synthesized in electric-arc plasma and activated in HF discharge (IV)

Type of catalyst	Converted gas composition (vol.%)				CH_4 conversion rate, η (%)	Catalyst performance[a]	Catalyst efficiency, η_{eff} (%)
	CO_2	CO	H_2	CH_4			
I	13.0	3.9	63.7	19.3	80.6	1352	99.5
II	10.1	1.0	43.4	45.5	54.5	888	91.0
III	13.0	3.7	63.1	20.2	79.8	1335	98.5
IV	13.5	4.1	64.0	18.4	81.0	1459	99.8

[a] $G \times 10^3$ $(m^3_{(CO+H_2)}\, m^{-1}_{cat})$.

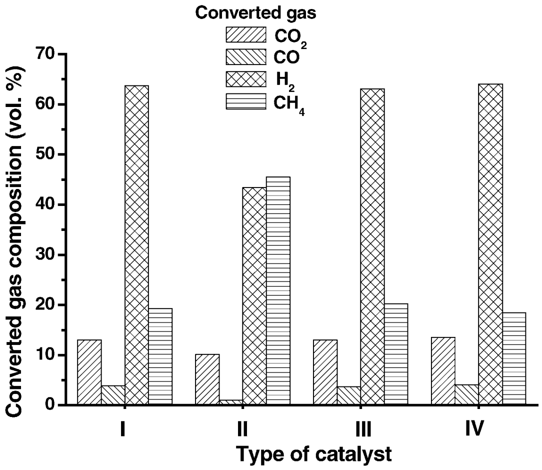

Fig. 7. Converted gas composition (vol.%) vs. of type of catalyst: I – conventional G 56A catalyst; II – regenerated in thermal plasma catalyst; III – synthesized in thermal plasma catalyst; IV – synthesized in thermal plasma and activated in HF discharge.

4. Conclusion

We studied the processes of plasmachemical synthesis and/or regeneration in electric-arc thermal plasma of catalysts that find application in the steam conversion of methane; depending on the plasmachemical process parameters and on the type of plasmachemical reactor (CW or WW), we produced samples whose specific surface reached 120 $m^2 g^{-1}$. Further, we determined the equilibrium parameters of the multi-component heterogeneous system Ni–Al–O–Ca–Mg for four different variants of the initial ingredients content at a pressure of 0.1 MPa and in the temperature range 1000–3700 K.

We carried out a comprehensive physical–chemical analysis of the plasmachemically synthesized and/or regenerated samples by using X-ray diffraction, electron microscopy, chemical, etc., analyses; thus, we explored the dynamics and kinetics of the samples' active surface formation by reduction and determined their activity (degree of CH_4 conversion, catalysts' efficiency). The plasmachemically synthesized and/or regenerated samples exhibited homogeneous chemical composition, analogous to that of the conventional industrial catalyst produced by Girdller, USA.

The results of the studies on the dynamics and kinetics of the plasmachemically synthesized and/or regenerated catalysts for steam conversion of methane showed that the electric-arc thermal plasma creates conditions for the production of catalyst compositions that are reduced 2–4 times as fast as their industrial analogs; moreover, when the reduction is carried out in HF discharge, the rate of the topochemical reduction rate exceeds that of the NDPC by about 10%.

The catalysts synthesized in a CW PCR have lower activity than their industrial analog G 56A; the catalysts synthesized in a WW PCR have activity comparable to that of the catalysts G 56A and G 56H used in the industry (HIMKO, Vratsa); indeed, when prepared under certain technological conditions (heterogeneous catalytic interaction between methane and steam in HF discharge) they are more active by about 10%.

References

[1] G.P. Vissokov, Applied Plasma Chemistry (Part 1), Tekhnika Publisher, Sofia, 1984, p. 295.
[2] G.P. Vissokov, Applied Plasma Chemistry (Part 2), Tekhnika Publisher, Sofia, 1987, p. 325.
[3] G.P. Vissokov, P.S. Pirgov, Nano-dispersed Powders: Plasma-Chemical Obtained and Properties, Poloprint, Sofia, 1998, p. 396.
[4] G.P. Vissokov, D.Sc. Thesis, Institute of Electronics, Bulgarian Academy of Sciences, Sofia, 1994.
[5] G.P. Vissokov, Bulg. Patent 35 353 (1982).
[6] G.P. Vissokov, Bulg. Patent 35 481 (1983).
[7] G.P. Vissokov, Ch. Jun Liu, Bulg. Chem. Ind. 72 (2001) 96.
[8] Ch. Jun Liu, G.P. Vissokov, B.W.-L. Lang, Catal. Today 72 (2002) 173.
[9] M.B. Kizling, S.G. Jaras, Appl. Catal. A 147 (1996) 1.
[10] P.N. Tsibulev, D.Sc. Thesis, Institute of General and Inorganic Chemistry, Ukraine Academy of Sciences, Kiev, 1996.
[11] G.P. Vissokov, Bulg. Chem. Ind. 55 (1983) 164.
[12] G.P. Vissokov, J. Mater. Sci. 27 (1992) 5561.
[13] G.P. Vissokov, Latv. J. Chem. 6 (1992) 662.
[14] G.P. Vissokov, J. Mater. Sci. 23 (1993) 6457.
[15] G.P. Vissokov, Bulg. Chem. Ind. 67 (1996) 42.
[16] G.P. Vissokov, Bulg. Chem. Ind. 67 (1996) 64;
G.P. Vissokov, Eng. Phys. J. 70 (1997) 609.
[17] P.S. Pirgov, G.P. Vissokov, Bulg. Chem. Ind. 69 (1998) 9.
[18] G.P. Vissokov, P.S. Pirgov, Appl. Catal. A: Gen. 168 (1998) 229.
[19] G.P. Vissokov, Com. Dept. Chem. BAS 32 (2000) 254.
[20] G.P. Vissokov, M. Panayotova, Catal. Today 72 (2002) 213.
[21] G.P. Vissokov, Catal. Today 72 (2002) 197.
[22] G.P. Vissokov, in: Proceedings of the VIth International Symposium on Heter. Catal., Part 2, Sofia, 1987, p. 303.
[23] G.P. Vissokov, in: D.S. Karpuzov (Ed.), Nova Sci. Publ., USA, 1996, p. 41.
[24] G.P. Vissokov, in: Proceedings of the International School seminar on "Electric-arc plasma in technology processes", Minsk, Belarus, 2–6 October, 1995, p. 49.
[25] G.P. Vissokov, Preprint, 45 (3), Am. Chem. Soc., Div. Pet. Chem., Washington, 2000, p. 396.
[26] G.P. Vissokov, in: Proceedings of the Ninth International Symposium on Heter. Catal., Varna, 23–27 September, 2000, p. 579.
[27] G.P. Vissokov, in: Proceedings of the Ninth International Symposium on Heter. Catal., Varna, 23–27 September, 2000, p. 585.
[28] G.P. Vissokov, in: Proceedings of the Ninth International Symposium on Heter. Catal., Varna, 23–27 September, 2000, p. 591.
[29] G.P. Vissokov, Plasma Sci Technol. 6 (2002) 1551.