The catalytic effect of plasma sprayed coatings for improved combustion of gaseous fuels

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Abstract
The article presents methods for reducing CO emissions and other toxic pollutants from combustion processes, emphasising the effect of catalysts to reduce such emissions. One of the most frequently used methods for reducing pollutants is the non-selective reduction of nitrogen oxides, which can be carried out in the presence of catalysts. This method uses CO from carbon-containing fuel combustion to reduce nitrogen oxides. However, this process is much more efficient in the presence of catalysts. The processes of catalytic CO combustion and NO_x reduction were carried out in a model chamber by burning natural gas. The results show the catalytic effect of plasma sprayed ceramic coatings on the catalysts and surfaces bounding the combustion spaces on the exhaust gas parameters.

The measurements of the natural gas combustion process parameters in the presence of the catalytic coatings showed that the coating based on a mixture of cerium oxide (CeO_2) had the greatest reduction effect, and the coating based on the mixture of vanadium oxide (V_2O_5) had a smaller impact on reducing carbon monoxide amounting to approximately 60%, and a nitrogen oxides reduction rate of 35%. In contrast, the CO reduction rate for the catalysts without the coating was 3%, and the degree of NO_x reduction was approximately 6%. The obtained results confirm the desirability of the catalyst coating application for CO combustion and NO_x reduction.

Catalytic coatings sprayed in multi-layer coating systems can be applied not only on the surfaces of catalysts but also on the surfaces of heating devices, and they may not only have a catalytic effect but can also extend the service life and improve the heating efficiency, which confirms the scope and purposefulness of using the plasma sprayed coatings.

Keywords
catalytic impact; plasma ceramic coatings

Introduction and Background Information

The basic process to obtain energy is the combustion of fuels. Regardless of whether we burn fossil or renewable fuels, pollutants are emitted into the atmosphere. For economic reasons, the combustion of conventional fuels is profitable and technologically simple. Nonetheless, the combustion of conventional fuels places a heavy burden on the environment due to emissions and a surplus carbon dioxide (CO_2) balance. Emissions might be improved by using primary or secondary methods of purification and the elimination of pollution, but such solutions are rather expensive. It is also obvious that fossil fuels will eventually be depleted. Therefore, one of the alternatives is to use biofuels, which are renewable fuels with lower economic parameters; that is why they are increasingly used in the energy sector. The CO_2 balance for the combustion process of biofuels is zero and is therefore well balanced. The process also emits fewer pollutants due to the lower combustion temperature and lower concentration of nitrogen oxides (NO_x), but unfortunately, complex organic compounds (including PAHs) are produced. When biofuels are burned, certain amounts of alkali metals and chlorine are released into the exhaust gases, which, when combined with sulphur and nitrogen oxides, create a highly corrosive atmosphere. In a result, combustion chambers and other metallic elements of the combustion devices degrade several times faster than when burning traditional fuels (Król, Łach, & Poskrobko, 2010; Sala, 2017; Tomaszek, 2019). There is another unfavourable aspect of using biofuels. Namely, some arable land needs to be devoted to their production where more food crops could be produced, while biofuel plants could grow in contaminated areas, but these areas are limited. This problem is important because it is not yet fully known how to deal with heavy metals and other toxins that absorbing plants consume when growing in contaminated areas. These harmful compounds will be partially released into the atmosphere along with the dust during combustion, and the rest will remain in the ash. Hence, when we take into account all the aspects of commercially available fuels, the process worth noting is the co-combustion of conventional fuels with biofuels, thus achieving a compromise between ecology and economy (Rudnev et al., 2011; Sala, 2017).

Over 4.5 million tonnes of gaseous pollutants and other volatile wastes have been emitted in Poland over the past year, of which only 15% has been neutralised (Malinowski & Chwiałkowski, 2017; Zajemska, Rajca, Szwaja, & Morel, 2016). Losses due to the emissions of air pollutants constitute up to 17% of the national income (Tomaszek, 2019). Professional power engineering and transport are the most burdensome for emissions. About 14% of Poland are areas with high emissions where fuel combustion is the main source of pollution. In Poland, permissible pollutant emissions have been set only for boilers, and their values are automatically transferred to industrial furnaces and municipal furnaces, taking into account only the thermal power of the device itself and not the processes that occur in this device. The penalties for exceeding the permissible emissions cover only 10% of the actual losses incurred by the economy. One of the first identified pollutants from combustion due to its highly toxic effects on the environment was carbon monoxide. In addition to CO, the basic impurities include sulphur oxides (SO_x), nitrogen oxides (NO_x), hydrocarbons (C_xH_y), carbon black (C_s), dust, tar and organic microparticles (Król et al., 2010; Tomaszek, 2019).

According to the principles of burning fuels, which include carbon, almost all of this element passes through the CO stage. For these reasons, technical efforts and all technologies are aimed at accelerating its total oxidation to CO_2 rather than limiting its formation in the combustion process, which would significantly reduce the amount of heat energy obtained in the combustion process and cause no unnecessary increase in costs. Significant improvement in the negative environmental impact of coal combustion processes can be achieved by (Tomaszek, 2019):

- dissemination of coal enrichment technologies,
- introduction of fluidised bed installations into operation,
- introduction of coal gasification with desulphurisation technology,
- dissemination of multi-zone dust burners with low NO_x emissions,
- dissemination of devices and technologies for SO_x, NO_x removal from flue gases.

The most commonly used method to reduce pollution is the non-selective reduction of NO_x, which uses the carbon monoxide remaining after the combustion process. The process takes place spontaneously without the participation of catalysts in specific temperature conditions and in the absence of oxygen in the zone where this phenomenon occurs. However, in the presence of catalysts, this process occurs much more efficiently, even in a zone with a lower temperature, highly reducing the amount of CO and NO_x, and instead of these oxides, N_2 and non-toxic CO_2 are released into the atmosphere. This method is expensive due to the use of catalysts based mainly on platinum, rhodium or palladium. Nonetheless, also transition metal group IV oxides can be used as catalysts, which are much cheaper, but there is a problem with the deposition of oxide layers on the catalyst surface where high purity of the deposited oxides is required, and these oxides are not resistant to abrasion (Magdziarz, Wilk, & Straka, 2017; Materazzi, Lettieri, Taylor, & Chapman, 2016; Morel, Jasinski, Zloto, & Stryjewski, 2015).

According to the theory of active complex catalysis (called the transition state theory), the mutual collision of active molecules easily occurs on the walls bounding the reaction-combustion space, and the reaction chains are shorter when the ratio of the surface area limited by the walls to the volume of the reaction space is greater. Therefore, catalysts should have the largest possible surface development, which significantly contributes to the intensification of catalysis. The process of catalysis efficiency improvement is mainly about choosing the right type of catalyst. Hence, the method of plasma spraying of catalytic coatings allows the possibilities of using catalysts for clean combustion to be expanded, especially in cases when, for economic or technical reasons, it is impossible to use appropriate catalysts (Pranevicius, Pranevicius, Valatkevicius, & Valincius, 2000).

It is widely known that plasma is the IV state of matter and has many properties used in gas combustion technology. Plasma is an ionised gas that conducts electricity and is thus capable of absorbing energy from electric or magnetic fields and transforming it into a stream of ionised gas. In plasma conditions, bi-directional reversible processes of dissociation and ionisation take place during the plasma formation stage, followed by recombination and association after plasma outflow. In such conditions, the energy absorbed by the plasma is released, and high-temperature gas is formed. It is generally accepted that the temperature of low-temperature plasma can reach a value of up to 50 000 K, unlike high-temperature plasma reaching a value of several hundred million degrees (Krylow, 1967; Morel et al., 2015; Pranevicius et al., 2000). Among the many methods of plasma generation, the stabilised arc discharge method is widely used, occurring at high currents and several dozen volts in the plasma torch chamber. By increasing the current density, together with simultaneous preventing the arc column from expanding, it is possible to transition from free arc discharge to air stabilised arc discharge. In the arc discharge column, which burns between the internal cathode and the plasma torch anode, a stabilised arc discharge is created at the appropriate pressure of the gas flow, causing thermal dissociation and ionisation of the gas. Ionised gas flows out of the hole in the anode and creates plasma. Next, the powder coating material is introduced into the plasma torch and flows at high speed through the nozzle. The coating material melts in the hot plasma stream, creating a cloud of liquid or semi-liquid droplets, which hit the substrate and deposit a layer. The bonds between the drops of coating material solidifying on the substrate have an adhesive type; however, adhesive-diffusion bonds form over time. When creating a coating from a "self-binding" material, for example, molybdenum, nickel and chromium alloy, a coating with strong diffusion bonding to the substrate is formed, which acts as a binding layer interface between the metal substrate and the protective ceramic coating (Dosta et al., 2016; Morel et al., 2015; Snapkauskiene, Valincius, & Grigaitien, 2012).

A coating means a multi-layer, multi-functional system characterised by the desired technical application and tailored strength, optical and chemical properties, also including catalytic ones. As a result, by proper selection of the type of coating material and the spraying parameters, a multi-layer coating is created, which allows many requirements to be achieved simultaneously, such as (Morel et al., 2015):

- wear resistance of the sprayed element by applying coatings with high hardness and high resistance to corrosion, cavitation, abrasion and erosive wear;
- desired heat transfer of the coatings and elements by applying materials with high absorbance and thermal conductivity,
- catalytic effect on chemical processes, including the combustion and afterburning of fuels, as well as the selective and non-selective reduction of nitrogen oxides.

It should be emphasised that the plasma spraying technique can produce coatings of various materials, the surface shape of the coatings, number of layers and thus give the coating a set of properties adequate to the operating parameters of the elements. Coatings can be sprayed on any materials (metallic alloys, ceramics, glass, etc.) where the surface is properly prepared by, for example, substrate cleaning, degreasing, blasting. It is also possible to produce coatings on chosen areas of entire surfaces of the elements, with simultaneous prevention of overheating of the sprayed surface. This technique also allows the coating of the elements of industrial facilities without disassembly. In almost every industry in which plasma sprayed coatings were used, improvement of the sprayed elements was obtained by increasing their operation time, quality of work, thermal efficiency and reducing pollution (Pranevicius et al., 2000). Plasma sprayed coatings of flame-retardant materials with high hardness for the walls of furnaces, furnaces, heat exchangers, and other industrial devices limit the processes of abrasion and wear of the sprayed equipment components and catalytically affect the combustion and afterburning processes of fuels. Studies conducted by the authors in the field of catalysing the afterburning of exhaust gases and processes reducing NO_x emissions might have a significant contribution to improving environmental conditions (Krylow, 1967; Muneer & Nadeera, 2018). They are conducted in terms of the needs of industry, including energy, metallurgy, municipal economy and transportation. To apply the catalytic coatings, a plasma arc gun with an internal arc was used, generating a plasma flux at a temperature of about 15 000 K, allowing all the materials used in the studies to be melted and coatings with the required strength and wear properties to be obtained (Krylow, 1967; Yu, Chen, He, & Yan, 2015).

The desirability of using catalysts

Catalysts work by reducing the activation energy of the reaction, which is expressed in the fact that in their presence, the reactions occur at an increased speed (at a constant temperature) or, which is important especially in flue gas ducts - the reactions can take place at a lower temperature. In the presence of a catalyst, the activation energy is significantly lower than the activation energy of a non-catalysed reaction. Nevertheless, catalysts do not affect the energy of the reactants or the reaction products and do not cause changes in enthalpy or thermodynamic potential. Metal catalysts - platinum or palladium, or rhodium catalysts are commonly used. Catalysts made of transition metal oxides (group IV) are produced less often, are cheaper and more resistant to poisoning by sulphur oxides than metal catalysts (Vasilyeva, Rudnev, & Tsvetnov, 2015; Yu et al., 2015). Oxidation reactions occurring on oxide catalysts occur in such a way that the oxidisable compound (CO, C_xH_y, C_s) first reacts with the surface oxygen of the catalyst, reducing the catalyst and then re-oxidising the previously reduced catalyst surface (Cao et al., 2012; Lukiyanchuk et al., 2013). The cited mechanism is particularly useful for describing oxidation reactions occurring on plasma-sprayed transition metal oxide catalysts (with the addition of hard-melting cermet materials). These catalysts are characterised by high surface development (5x relative to the surface resulting from the geometric dimensions) due to surface roughness (R_a) of about 60 μm. The roughness of the catalyst surface promotes both an increase in the rate of chemical reactions as well as heat absorption, which can lead to a reduction in their dimensions (Ai et al., 2018; He, Fan, Bellettre, Yue, & Luo, 2020).

Hydrogen, carbon monoxide and hydrocarbon oxidation catalysts materials

Platinum, palladium and nickel (used for O_2-H_2 fuel cells) have a catalytic effect on hydrogen oxidation processes. The oxides of periodic table period IV also have catalytic properties, in particular cobalt, copper and nickel. The activation energy of H_2 oxidation in the presence of these oxides is from 45 to 100 kJ/mol, and a reaction order from 0.5 (Cr_2O_3) to 1 (Co_3O_4) (Ai et al., 2018; Chen et al., 2018; Zhang, Jiang, & Shangguan, 2016). Of course, the most active are oxides in the presence of which the 1st order reaction takes place. Figure 1 shows the relationship of the logarithm of the constant rate (curve 1) and the energy of activation for period IV oxides (curve 2) on the course of the H_2+O_2 reaction (Pranevicius et al., 2000; Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006; Zhang et al., 2016).
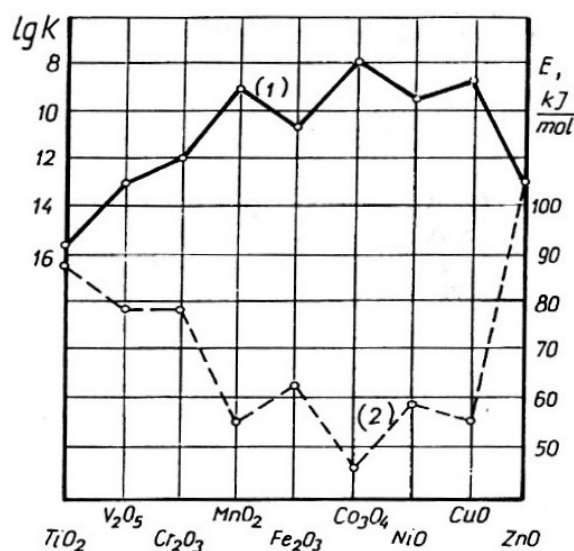

Figure 1. Logarithm dependence of H_2+O_2 reaction constant rate (curve 1) and activation energy (curve 2) for periodic table period IV elements at 325°C (Pranevicius et al., 2000)

Platinum and palladium also show high activity in carbon monoxide oxidation. In the presence of these metals, already at the temperature of 470°C, 100% combustion of CO occurs in an oxygen atmosphere (Lee et al., 2020; Wang, Duan, & Ye, 2018; Zhong-yu et al., 2016). These oxides, i.e. group IV of the periodic table, also catalyse CO oxidation; however, a higher temperature process is required, and the reaction takes place at a slower speed. During the catalytic combustion of CO in the presence of nickel oxide, it was found that oxygen is absorbed on the surface of the catalyst to form an O^- ion, which then reacts with the absorbed CO. Figure 2 shows the dependence of the change in the logarithm of catalytic activation of group IV oxides on the oxidation rate of the CO+O_2 reaction (Celik, Ozdemir, Avci, & Tsunekawa, 2005; Pranevicius et al., 2000; Zhang et al., 2016).
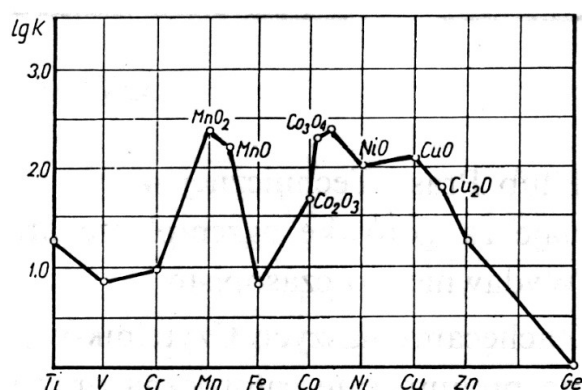
Figure 2. Logarithm dependence of period IV metal oxides catalytic activation for CO+O₂ oxidation reaction (Pranevicius et al., 2000)

The most active oxides are cobalt, copper, manganese and nickel, while the oxides of zinc, titanium, vanadium and iron have low catalytic activity. Significant technical applications were found for CuO, NiO and MnO_2. For these oxides, the activation energy for CO oxidation (at normal temperature) is from 12.5 to 25 kJ/mol and 62 - 110 kJ/mol at a temperature of 470 – 670°C (He, Tan, Wang, Xu, & Hong, 2014; Kim, Hwan, Hong, Park, & Lee, 2017; Osipov et al., 2016). Furthermore, lanthanide oxides reduce the activation energy of the CO oxidation process, with their ordering in a decreasing direction of activity as follows: CeO_2, La_2O_3, Nd_2O_3, Dy_2O_3. CeO_2 is mostly applied in the form of a mixture with Al_2O_3 in a ratio of 3:4, which catalyses CO oxidation already at 475°C, and it is worth remembering that conducting combustion at moderate temperatures has a positive effect on reducing the NO_x content in exhaust gases (He et al., 2020; Morel, 2012; Pranevicius et al., 2000). The oxidation of hydrocarbons is strongly influenced by cobalt, nickel and copper oxides. Due to the symmetrical structure, for example, CH_4, its oxidation is a difficult process, and the greatest catalytic capacity was demonstrated by Co_3O_4, NiO, CuO and MnO_2. In addition, cerium and terbium oxides have a high methane oxidation capacity (He et al., 2020; Morel, 2011, 2012; Qiao, Wang, Weng, Liu, & Li, 2018).

Investigation on the effect of ceramic coatings on catalysation of CO afterburning and NO_x reduction in natural gas exhaust fumes

The study was conducted in four stages, determining the effect of three types of catalytic plasma sprayed coatings on the catalytic converter and the catalytic converter itself and on the post-combustion of CO and NO_x in natural gas exhaust flowing through the catalytic channel. Because the catalytic converter introduced large turbulences in the exhaust gas flow and acted as a heat accumulator, maintaining a higher temperature along its length, compared to the duct without the converter, it could affect the kinetics of the CO-NO_x reaction. The tests were carried out on a measuring stand constructed of a ceramic, cylindrical combustion chamber (1) – 7000 mm long; a burner (2) – in which natural gas was burned, with a burner converter and rim (3) – which was mounted with the chamber into the construction of the device (4). The air and natural gas introduced into the combustion chamber were measured by rotameters (5, 6) and regulated by valves (10). Inside the ceramic chamber, at a distance of about 4000 mm from the burner, there was a metal catalyst 1000 mm long, on whose surface the catalytic coatings were sprayed. The composition and combustion parameters were measured before and after the catalyst converter using a probe (18) and a Teseto 350 analyser (12). Every 500 mm along the entire length of the chamber, thermocouples (13) were installed, allowing measurement of the temperature distribution in the chamber. In order to ensure a constant and unchanging gas flux, the gas flowed through a gas regulator (7) and in the case of air combustion, it flowed through an intermediate tank (8), which played the role of a buffer eliminating airflow fluctuations that were introduced to the burner by a fan (9) and burned in a ceramic chamber.

The conducted tests consisted of exhaust gas composition analysis before and after the catalyst converter was sprayed with three different oxides: vanadium (V_2O_5), cerium (CeO_2) and manganese (MnO_2) oxide, in thermodynamic equilibrium for three excess air coefficients α = 1.02, 1.05, and 1.08. After supplying air and gas and igniting the burner, the chamber was heated for a period of 200 – 300 minutes to a state of thermal equilibrium, which was determined by using the thermocouples. The schematic view of the combustion stand is shown in Figure 3.
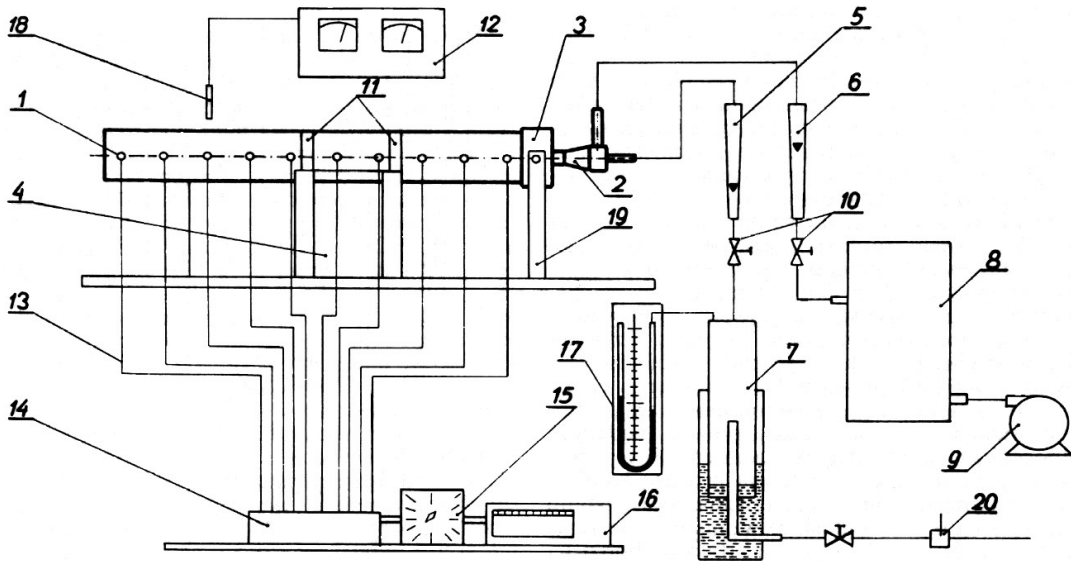
Figure 3. Test stand for measuring gas burning process parameters (Pranevicius et al., 2000)
1 – burning chamber, 2 – burner, 3 – burner rim, 4 – construction,
5 – gas rotameter, 6 – air rotameter, 7 – gas regulating vessel, 8 – air tank, 9 – fan,
10 – rotameter valves, 11 – clamp hoop, 12 – combustion gas analyser,
13 – thermocouple, 14 – thermostat, 15 – thermocouple switch, 15 – recorder,
17 – U-tube, 18 – gas sampling probe, 19 – burner stand, 20 – gas valve, G – gas, P – air

The temperature was measured at 12 points along with the chamber during 5 subsequent measurements (every 15 minutes), which allowed identification of the state of equilibrium of the system and commencement of measurements of the exhaust gas composition before and after the catalyst converter. Exhaust gas composition analyses performed before and after the catalyst converter were recorded in five consecutive series (they did not differ by approximately 5%). The average values were calculated from the data, and the results were entered in the table.

Nonetheless, when the results of subsequent measurements differed from each other, three more series of measurements were carried out, the two extreme pairs of results were rejected, and the remaining arithmetic mean value was calculated.

The analysis of the exhaust gas composition consisted in determining:
- the percentage of oxygen in the exhaust gas,
- the concentration of NO_x and CO in ppm,
- the exhaust gas temperature at the place of intake and at ambient temperature.

Results and discussion

The CO_2 content in the exhaust gas was calculated by the analyser according to the algorithm written in it and was a function (this value was treated as an auxiliary parameter) determining the quality of the combustion process. In the first stage, the impact of the catalytic converter covered with a plasma neutral coating of aluminium oxide on the process of carbon monoxide after burning and reduction of nitrogen oxides was determined; this effect turned out to be minimal and is shown in Table 1, Figures 4 and 5. For the excess air coefficient of $\alpha = 1.02$, there was no decrease in the oxygen content in the exhaust gas; the oxygen content in the exhaust gas before the catalyst and after the catalyst was constant at 0.5%, the CO reduction was 2.5%, which corresponded to a decrease from 554 ppm before to 540 ppm after the catalyst and the NO_x reduction ratio was 5.9%, which corresponded to decrease from 170 ppm to 160 ppm before and after the catalyst. The results for $\alpha = 1.05$ excess air coefficient showed no decrease in the oxygen content in the exhaust gas either; the oxygen content in the exhaust gas before and after the catalyst was constant (1.1%), the CO reduction was 3.3%, which corresponded to a decrease from 316 ppm to 260 ppm, respectively before and after the catalyst and the NO_x reduction ratio was 6.5%, which corresponded to a decrease from 182 ppm to 170 ppm, respectively before and after the catalyst. For excess air coefficient $\alpha = 1.08$, there was no decrease in the oxygen content in the exhaust gas either; the oxygen content in the exhaust gas before the catalyst and after the catalyst was constant (1.5%), the CO reduction was 21%, which corresponded to a decrease from 70 ppm before the catalyst to 55 ppm after the catalyst, and the NO_x reduction ratio was 11%, which corresponded to a decrease from 135 ppm to 120 ppm before and after the catalyst, respectively. The quite large values of the reduction coefficient for carbon monoxide and nitrogen oxides occurring, in this case, result from the measurement error of the analyser

measuring the exhaust gas composition for low contents of carbon monoxide and nitrogen oxides. It is supposed that such a large metal converter could affect the combustion processes of carbon monoxide in exhaust gases, while its real impact was within the limits of the measurement error. The fact that there were no post-combustion or reduction processes here is evidenced by the constant oxygen content in the exhaust gas and a large decrease in the exhaust gas temperature in the converter space.

Table 1. Measurement results of exhaust gas composition for the channel with catalytic converter without catalytic coating

Flue gas parameters	Before converter	After converter	Before converter	After converter	Before converter	After converter
Excess air coefficient α	1.02		1.05		1.08	
O_2 [%]	0.5	0.5	1.1	1.1	1.5	1.5
CO_2 [%]	11.7	11.7	11.4	11.4	11.0	11.0
CO [ppm]	554	540	316	260	70	55
CO reduction rate	R_{CO}= 2.5%		R_{CO}=3.3%		R_{CO}=21%	
NO_x [ppm]	170	160	182	170	135	120
NO_x reduction rate	R_{NO}=5.9%		R_{NO}=6.5%		R_{NO}=11%	
Flue gas temperature [°C]	835	815	855	830	844	820
Ambient temperature [°C]	25	25	25	25	25	25

In the second stage of the study, the influence of the catalytic coating based on vanadium oxide with an appropriately selected activator on the combustion of carbon monoxide and non-selective reduction of nitrogen oxides was found to be significant (Table 2; Figs. 4 and 5). For the excess air coefficient of α =1.02, there was a slight decrease in the oxygen content in the exhaust gas of the catalyst from 0.7% before to 0.4% after the catalyst, the CO reduction was 60%, which corresponded to a decrease from 570 ppm before to 225 ppm after the catalyst and the NO_x reduction ratio was 39%, which corresponded to a decrease from 180 ppm before to 110 ppm after the catalyst. However, for excess air ratio α =1.05, there was a decrease in the oxygen content in the exhaust gas before the catalyst from 1.1 % to 0.7% after the catalyst, the CO reduction was 89%, which corresponded to a decrease from 310 ppm to 35 ppm before and after the catalyst, respectively, and the NO_x reduction rate was 37%, which corresponded to a decrease from 200 ppm before to 127 ppm after the catalyst. The values of the CO and NO_x reduction rates for excess air coefficient α =1.07 are burdened with an error resulting from the limited measuring accuracy of the analyser for such small values and were: the CO reduction rate was 88%, which corresponded to a decrease from 80 ppm before the catalyst to 50 ppm after the catalyst and the NO_x reduction ratio was 55%, which corresponded to a decrease from 131 ppm to 99 ppm before and after the catalyst, respectively, while the oxygen content in the exhaust gas dropped from 1.5% to 1.3%, respectively before and after the catalyst. The analysed processes of catalytic combustion of carbon monoxide and non-selective reduction of nitrogen oxides are evidenced by an oxygen content decrease in the exhaust gas and a decrease in the content of nitrogen oxides, which were reduced by the afterburning of carbon monoxide, whose content in the exhaust gas before and after the catalyst also decreased. As a result of the combustion of carbon monoxide, the heat was generated, which was absorbed by the exhaust gases as evidenced by the constant temperature in the catalyst space and even an increase for excess air coefficient α = 1.05.

Table 2. Measurement results of exhaust gas composition for the channel with catalytic converter sprayed with a coating based on V_2O_5 with activator

Flue gas parameters	Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Excess air coefficient α	1.01		1.05		1.07	
O_2 [%]	0.7	0.6	1.1	0.9	1.5	1.3
CO_2 [%]	11.7	11.8	11.4	11.5	11.0	11.1
CO [ppm]	570	225	310	35	80	10
CO reduction rate	R_{CO}=60%		R_{CO}=89%		R_{CO}=88%	

NOx [ppm]	180	110	200	127	131	59
NOx reduction rate	R_{NO}=39%		R_{NO}=37%		R_{NO}=55%	
Flue gas temperature [ºC]	830	829	862	863	854	854
Ambient temperature [ºC]	26	26	26	26	25	26

In the third stage, the influence of the cerium oxide-based catalytic coating with activator on the combustion of carbon monoxide and non-selective reduction of nitrogen oxides was examined, which was the largest (Table 3; Figures 4 and 5). For the excess air coefficient of α =1.04, the oxygen content in the exhaust gas dropped from 0.8% to 0.2% before and after the catalyst, and the CO reduction was 60%, which corresponded to a decrease from 564 ppm before to 205 ppm after the catalyst, and the NOx reduction ratio was 38%, which corresponded to a decrease from 185 ppm before to 115 ppm after the catalyst. Nevertheless, for excess air coefficient α =1.04, the oxygen content in the exhaust gas before the catalyst dropped from 1.0% to 0.6% after the catalyst, the CO reduction ratio was 95%, which corresponded to a decrease from 312 ppm to 15 ppm before and after the catalyst, respectively, and the NOx reduction ratio was 36%, which corresponded to a decrease from 211 ppm to 135 ppm before and after the catalyst, respectively. The values of the CO and NOx reduction rates for excess air coefficient α =1.08 are burdened with an error resulting from the limited measuring accuracy of the analyser for such low values and were as follows: the CO reduction rate was 88%, which corresponded to a decrease from 80 ppm before to 10 ppm after the catalyst and the NOx reduction ratio was 55%, which corresponded to a decrease from 129 ppm before to 63 ppm after the catalyst, while the oxygen content in the exhaust gas of the catalyst dropped from 1.6% down to 1.2%. The catalytic afterburning of carbon monoxide and non-selective reduction of nitrogen oxides for this type of catalyst was demonstrated by a decrease in the oxygen content in the exhaust gas and a decrease in the content of nitrogen oxides which were reduced by carbon monoxide afterburning, whose content in the exhaust gas before and after the catalyst also decreased. After the combustion of carbon monoxide, the heat was generated and absorbed by the exhaust gas, resulting in a slight increase in the exhaust gas temperature in the catalyst space

Table 3. Measurement results of exhaust gas composition for the channel with catalytic converter sprayed with a coating based on CeO_2 with activator

Parameters	Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Excess air coefficient α	1.02		1.04		1.08	
O2 [%]	0.8	0.2	1.0	0.6	1.6	1.1
CO2[%]	11.6	11.9	11.3	11.6	11.1	11.4
NOx [ppm]	185	115	211	135	129	63
NOx reduction rate	R_{NO}=38%		R_{NO}=36%		R_{NO}=55%	
CO [ppm]	564	205	312	15	98	10
CO reduction rate	R_{CO}=60%		R_{CO}=95%		R_{CO}=88%	
Flue gas temperature [ºC]	834	829	852	853	831	830
Ambient temperature [ºC]	24	24	26	26	26	26

In the fourth stage of the study, the influence of manganese oxide with an activator contained in the catalytic coating was examined. The results are shown in Table 4, Figures 4 and 5. For the excess air ratio of α=1.01, there was a decrease in the oxygen content in the exhaust gas before the catalyst from 0.7% to 0.2% before and after the catalyst, respectively. The CO reduction rate was 56%, which corresponded to a decrease from 555 ppm before to 245 ppm after the catalyst, and the NOx reduction ratio was 47%, which corresponded to a decrease from 171 ppm to 91 ppm before and after the catalyst, respectively. However, for excess air coefficient α = 1.05, there was a decrease in oxygen content in the exhaust gas before the catalyst from 1.1% to 0.8% after the catalyst; the CO reduction rate was 90%, which corresponded to a decrease from 322 ppm to 32 ppm before and after the catalyst, respectively, and the NOx reduction ratio was 31%, which corresponded to a decrease from 207 ppm before to 141 ppm after the catalyst. The values of the CO and NOx reduction rates for excess air coefficient α = 1.09 are burdened with an error resulting from the limited measuring accuracy of the analyser for such small values and were: the CO reduction rate was 84%, which corresponded to a decrease from

80 ppm before the catalyst to 14 ppm after the catalyst and the NO_x reduction ratio was 52%, which corresponded to a decrease from 125 ppm before to 60 ppm after the catalyst, while the oxygen content of the exhaust gas before the catalyst dropped from 1.8% to 1.5% after the catalyst. The catalytic afterburning of carbon monoxide and non-selective reduction of nitrogen oxides for this type of catalyst were demonstrated by a decrease in the oxygen content in the exhaust gas and in the content of nitrogen oxides, which were reduced by the afterburning of carbon monoxide, whose content in the exhaust gas before and after the catalyst also decreased. After the combustion of carbon monoxide, the heat was generated and absorbed by the exhaust gas, which was identified by an almost constant temperature of exhaust gas in the catalyst space.

Table 4. Measurement results of exhaust gas composition for the channel with catalytic converter sprayed with a coating based on MnO_2 with activator

| Parameters	Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Air-fuel ratio α	1.01		1.05		1.09	
O_2 [%]	0.7	0.2	1.1	0.8	1.8	1.3
CO_2 [%]	11.7	11.8	11.5	11.6	10.9	11.0
CO [ppm]	555	245	322	32	90	14
CO reduction rate	R_{CO}=56%		R_{CO}=90%		R_{CO}=84%	
NO_x [ppm]	171	91	207	141	125	60
NO_x reduction rate	R_{NO}=47%		R_{NO}=31%		R_{NO}=52%	
Flue gas temperature [ºC]	835	835	855	854	844	842
Ambient temperature [ºC]	25	25	25	25	25	25
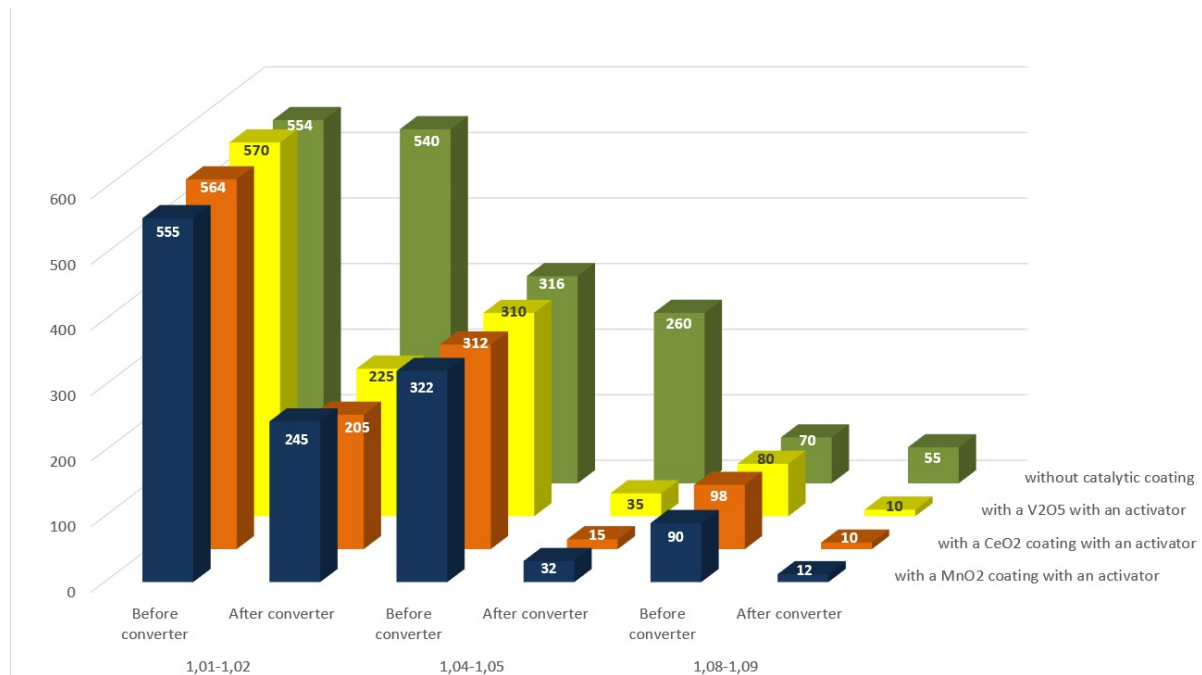
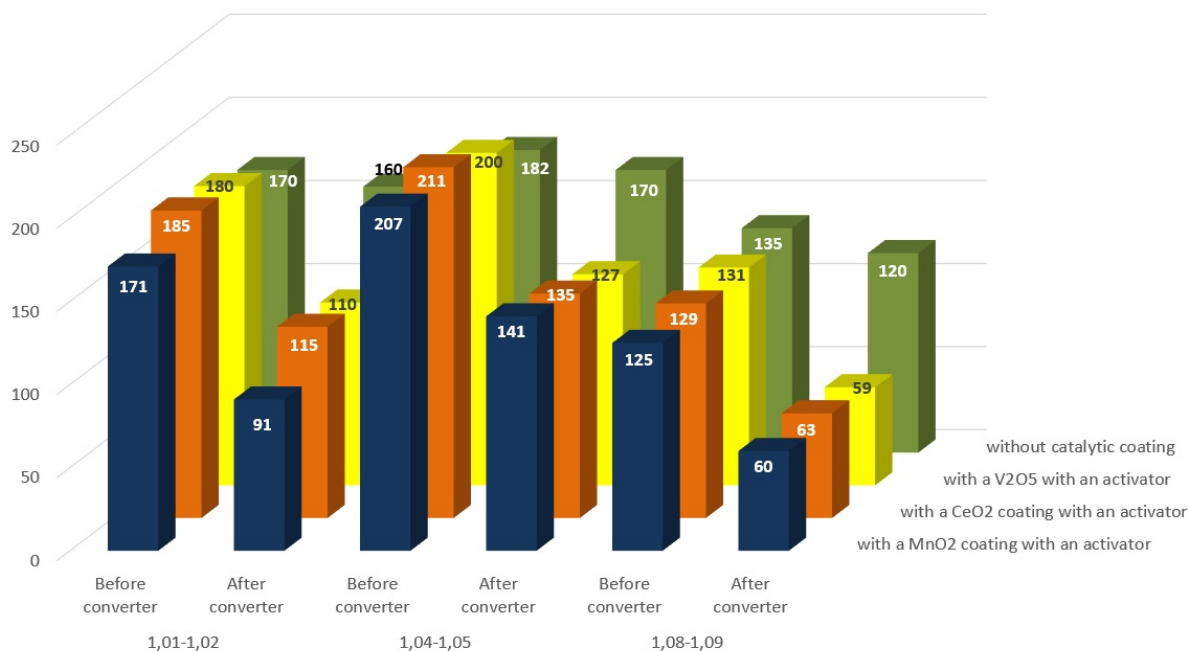*Figure 4. The concentration of CO in exhaust gases depending on the type of catalytic coating*

Figure 5. The concentration of NOₓ in exhaust gases depending on the type of catalytic coating

The authors plan to conduct research on other coatings with a catalytic effect on the post-combustion of CO and non-selective reduction of NOₓ both for liquid fuel, natural gas and biofuels. Perspective modernisation of the research stand will allow the authors to carry out the selective reduction of nitrogen oxides using biogas resulting from the decomposition of bio-waste as the reducer. This study is planned to be realised using the same catalysts used in the presented tests and other catalysts selected based on the authors' previous investigations.

Conclusions

1. The drop in gas temperatures in the space of the catalyst without a catalytic coating ranged from 20 to 25°C and was the highest for all the research stages, which indicates that the carbon monoxide afterburning process did not take place there. However, the drop in the flue gas temperatures in the space of the sprayed catalytic coating was of the order of 1°C for the coatings based on vanadium and manganese oxide, while for the cerium oxide coating, even a 1°C increase in the flue gas temperature after the catalyst was obtained.

2. This phenomenon can be explained by the combustion of carbon monoxide taking place in the space of the catalyst, with oxygen contained in non-selectively reduced nitrogen oxides and with the remaining oxygen in the combustion air exhaust gas (the remaining oxygen in the exhaust gas results from the excess air coefficient).

3. The decrease in the content of carbon monoxide and nitrogen oxides in the catalyst channel with a converter without a catalytic coating was small and resulted from spontaneous combustion processes of carbon monoxide and the thermal decomposition of nitrogen oxides. The decrease in the content of carbon monoxide and nitrogen oxides in the catalyst channel with the plasma sprayed body with the tested catalytic coating was significant, and it depended mostly on the type of coating that catalysed the combustion processes of carbon monoxide and non-selective reduction of nitrogen oxides.

4. The results of the natural gas combustion process measurements in the presence of the catalytic coatings used in the study indicated the highest efficiency of the coating formed on the basis of the CeO_2 oxide and activator mixture. Catalytic coatings included in multi-layer coating systems can be sprayed not only on the surfaces of catalytic converters but also on the surfaces of thermal devices and may affect not only catalysis but also the service life of devices due to the application of coating systems.

5. Plasma sprayed catalytic coatings have a much greater thickness compared to chemically or vacuum deposited layers and can be sprayed again in places where it has worn out without the need to disassemble the catalyst or thermal device on which the coating was sprayed.

6. The results of the measurements obtained at all stages of the study in which the coatings were used demonstrated the desirability of spraying catalytic coatings on the catalyst surfaces and other surfaces bounding the combustion chamber.

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