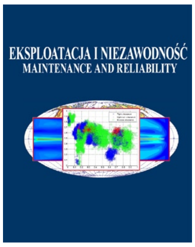

Eksploatacja i Niezawodnosc – Maintenance and Reliability

Volume 24 (2022), Issue 1

journal homepage: http://www.ein.org.pl

Article citation info:

Kruczyński SW, Orliński P, Ślęzak M. The comparative analysis of catalytic properties of Group 11 elements in NO$_x$ reduction by hydrocarbons in the presence of oxygen. Eksploatacja i Niezawodnosc – Maintenance and Reliability 2022; 24 (1): 170–176, http://doi.org/10.17531/ein.2022.1.19.

The comparative analysis of catalytic properties of Group 11 elements in NO$_x$ reduction by hydrocarbons in the presence of oxygen

Indexed by: Web of Science Group

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Highlights

- The structure of metal monolith models coated with the Al_2O_3-SiO_2 carrier was discussed.
- The surface topography of the Al_2O_3-SiO_2 carrier was assessed based on SEM images and acidity tests of its surface using the ammonia desorption method, including measurements of the specific surface using the BET method and porosity of the catalytic carrier using the BJH method.
- The results of NO_2, NO, and C_3H_6 conversion tests as well as CO and N_2O formation were analysed and assessed in the developed reactors located in an electric tubular furnace, depending on the NO$_x$ conversion temperature at a constant dose of the reducing agent (C_3H_6).

Abstract

NO$_x$ emission reduction in diesel engines can be achieved by using catalytic reactors reducing nitrogen oxides, including NH_3-SCR and possibly also HC-SCR reactors. Reactors using ammonia achieve large conversion rates but cause a lot of operational problems. For this reason, the interest in reactors using hydrocarbons and their derivatives to reduce NO$_x$ has increased. Such reactors are the ones using metals from Group 11 (coinage metals) such as Cu, Ag and Au placed on an Al_2O_3-SiO_2 carrier as active materials. The article characterizes the porosity and acidity of the carrier surface. Conversion of NO_2, NO and propene as well as the formation of CO and N_2O depending on the temperature at constant dosing of propene on a carrier covered with Cu, Ag and Au with a metal content of 4 g/dm^3 were evaluated. The results of the tests showed that the tested Group 11 elements can be the basis for further experiments related to the development of this exhaust fumes cleaning technology for diesel engines.

Keywords

Diesel engine, NO$_x$ reduction, conversion testing, Group 11 elements.

1. Introduction

Based on the analysis of the test results of diesel engines manufactured so far and the possibilities of development of their injection systems, it may be concluded that they meet the standards limiting the emission of carbon monoxide and hydrocarbons, while it is much more difficult to meet the requirements limiting the emission of particulate matter and nitrogen oxides [10, 11, 19]. The emission of nitrogen oxides, due to their toxic properties and large amounts emitted into the atmosphere, has become one of the main problems that need to be solved in future designs of these engines. The implementation of Euro 6 standard provisions in Europe since 2014 significantly reducing CO, THC, NO$_x$, PM and PN emissions in the LDV and HDV vehicle type-approval tests has forced vehicle manufacturers to significantly reduce emissions of harmful substances, including in particular NO$_x$ emissions. Therefore, research is being carried out on the creation, under laboratory conditions, of running cycles corresponding to the actual operation of vehicles so that actual emissions of harmful components into the environment, including in particular nitrogen oxides, could be assessed quickly and accurately [22].

The reduction of the NO$_x$ emissions of diesel engines can be achieved [11]:

- by methods applied inside the engine. These methods consist in conducting the processes occurring during the preparation and subsequent combustion of the mixture in such a way that the concentration of NO$_X$ in the exhaust gases of the engine could be as low as possible [24]. This process involves finding an optimum between engine power, specific fuel consumption and emissions of harmful substances,
- by using selective catalytic reduction reactors for nitrogen oxides, such as NH_3-SCR or possibly HC-SCR reactors,
- by using LNT reactors that selectively reduce nitrogen oxides, being NO$_x$ traps [11].

Exhaust fumes recirculation, when applied to an extent that does not significantly increase fuel consumption and PM emission, reduces the NO$_x$ emission to a small extent and is not sufficient to meet the requirements of Euro 6 and Euro VI standards. However, its application contributes to the reduction of NO$_x$ concentration upstream of the SCR reactors, thus facilitating their operation. Therefore, it is necessary to use the reactors for selective catalytic reduction of NO$_x$.

Nitrogen oxides in the presence of oxygen can be removed by selective chemical reduction, which can be divided into two groups, depending on the properties of the reducing agent:

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- ammonia reduction (NH_3-SCR)
- In the NH_3-SCR systems, gaseous ammonia can be released from ammonia sorbents or by ammonium salt decomposition and can be introduced into the exhaust gases at any temperature, especially at low loads of the combustion engine [9].
- In the case of SCR reactors active at a low temperature, NO_x emissions can be reduced at a temperature well below 200°C. $MgCl_2$ composites with various carbon materials, such as graphite or graphene can be used as ammonia sorbents [5].
- The commonly used method of ammonia supply to the NH_3-SCR reactor is the injection of an aqueous urea solution (AdBlue liquid), from which gaseous ammonia is obtained in hydrolysis and thermolysis processes [16]. The dimensions of sprayed AdBlue droplets have a fundamental impact on the efficiency of the selective catalytic reduction of NO_x [16].
- The hydrolysis of the aqueous urea solution may lead to the formation of poisonous sediments that may be problematic during the operation. Several combinations of urea decomposition reactions and sediment formation mechanisms are presented in the paper [2]. An important problem of effective NO_x reduction is the proper control of AdBlue fluid injection in an open loop or more precisely in a closed loop, taking into account the phenomenon of gaseous ammonia storage [23]. The most frequently used catalytically active materials are V_2O_5/TiO_2 or $V_2O_5/WO_3/TiO_2$ oxides. [25, 26]. Zeolites are also used as catalytically active materials in modern solutions. The problems with unburned hydrocarbons stored in large-pore zeolites have been an incentive to search for small-pore materials. Chabazite reactors were developed [4], containing Cu or Fe ions marked as Cu/SSZ-13 or Fe/SSZ-13, for NH_3-SCR catalysis applications. Despite these drawbacks and due to the high NO_x to N_2 conversion, these reactors are commonly used in LDV and HDV vehicles.
- the reduction with hydrocarbons (HC-SCR) or their derivatives containing oxygen, most often light alcohols. These reactors feature the following properties:
  - they achieve a relatively smaller conversion of NO_x not exceeding 80% [12],
  - NO_X conversion is achieved in a narrow range of high temperatures of 400–500°C [12],
  - they require high hydrocarbon doses due to their low selectivity and thus contribute to the heating of the reactor [7, 12]. It is often observed that the higher the dose of the injected hydrocarbons, the broader the range of the NO_x reduction temperature. A large dose of the injected hydrocarbons may increase the reactor temperature to values not encountered in oxidizing reactors used in diesel engines. The injection of 3% of the fuel dose upstream the HC-SCR reactor increases the temperature of the reactor bed by 30°C, and the injection of 6% of the fuel increases the temperature by 50°C.

Group 11 elements were considered catalytically active materials. Papers [15, 18] present the results of research on the use of copper ions placed in zeolites impacting their activity, depending on the oxygen content in exhaust fumes and the acidity of the reactor active surface.

Paper [17] compares the activity of the bimetal Ag-Au system on Al_2O_3, as compared to the activity of Ag on Al_2O_3, demonstrating that the activity of the Ag-Au bimetal is higher than either Ag or Au. On the other hand, the authors of the paper [3] found a promotional effect of hydrogen addition to propene in the Au/Al_2O_3 reactor. Paper [12] describes the preparation for obtaining the Ag/Al_2O_3 reactor and characterizes the porosity and acidity of its surface. The silver dispersion was assessed based on oxygen adsorption tests on silver crystallites and based on TEM images of silver crystallites. NO_2, NO and propane conversion was evaluated depending on the temperature. The conversion of NO_2, NO and propane at 500°C was also evaluated, depending on the added reducing agent and the selectivity of propane in the NO reduction.

Papers [7, 20] present the results of research concerning NO_x reduction with hydrocarbons and light alcohols on silver reactors. In order to increase the activity of the silver catalyst, the admixtures of MgO and CeO_2 oxides were added to the interlayer with Al_2O_3 [21]. Metal ion substituted zeolites are often used as active materials in HC-SC technology [15]. It was concluded that the most active HC-SCR catalysts should have strong acid locations, an active phase such as copper or cobalt, or element activity such as silver or a mixture of metals for the broader scope of activity. To reduce deactivation, materials should contain noble metals such as platinum or rhodium. Tests of the impact of hydrogen addition to different hydrocarbon reducing agents on the NO_x reduction efficiency were conducted both under laboratory experiments and in the engine dynamometer at a temperature below 315°C on the Ag/Al_2O_3 reactor with a 2.5% silver weight content [6]. Hydrogen increased the NO_x reduction efficiency at low temperatures (245–315°C).

The catalytic reduction of NO_x on the Ag/Al_2O_3 catalyst was also tested using such reactants as liquid hydrocarbons (GTL) and butanol [8]. It was proved that the effects obtained result from high reactivity, polarity and diffusivity of butanol in the catalyst, increasing the NO_x conversion.

In research works on increasing NO_x reduction activity, especially at low temperatures, the phenomenon of cold plasma was used. Thus, the efficiency of NO_x reduction using HC SCR technology with Pt- and Ag-based catalysts on an Al_2O_3 carrier at different temperature values was assessed using hydrogen and hydrocarbons as reducing agents supplied directly or generated on an engine station by plasma reforming [14]. The cold plasma produced in the corona discharge reactor was used to reform the diesel fuel for the selective catalytic reduction (HC-SCR) of NO_x on the Ag/Al_2O_3 catalysts [1].

2. Objective and scope of the works

The literature on the subject does not include the results of the tests of NO_x selective catalytic reduction with hydrocarbons using Group 11 elements applied on a carrier with high surface acidity. However, the acidity of the surface of the carrier [12] is specified in the literature as a factor contributing to the catalytic reduction of NO_x.

The objective of the paper is to assess and compare the catalytic activity of copper, silver and gold applied onto a carrier with high acidity in the selective catalytic reduction of NO and NO_2 with propene and additionally to compare the formation understood as the formation of undesired emission of N_2O and CO in actual exhaust fumes of a diesel engine containing large amounts of oxygen.

The work was carried out in the following stages:

- The structure of metal monolith models covered with the Al_2O_3-SiO_2 carrier.
- The assessment of surface topography of the Al_2O_3-SiO_2 carrier based on SEM images and acidity tests of its surface using the ammonia desorption method, including measurements of the specific surface using the BET method and porosity of the catalytic carrier using the BJH method.
- Impregnation of the carrier with selected Group 11 metals.
- The tests of NO_2, NO, and C_3H_6 conversion as well as CO and N_2O formation in the developed reactors located in an electric tubular furnace, depending on the NO_x conversion temperature at constant reducing agent dose (C_3H_6).
- Analysis of test results.

3. The structure of metal monolith models covered with the Al_2O_3-SiO_2 carrier

The monolith models were made of heat-resistant steel with a diameter Φ = 30 mm, a length L = 80 mm and with 400 cpsi cells, covered with aluminium polyphosphate. The carrier in the form of aluminosilicate with a content of 70% of Al_2O_3 and 30% of SiO_2 was then applied onto them using the sol-gel method.

Unfavourable transformation of active forms of γ-Al_2O_3 with a large surface to α-Al_2O_3 can be prevented by introducing elements or compounds thermally stabilizing aluminium oxides varieties into the carrier. Such a compound is SiO_2, which is formed by $Si(OC_2H_5)_4$ hydrolysis process [12]. An additional positive effect of the introduction of SiO_2 into the carrier layer may be an increase in the acidity of the carrier surface. The ceramic base layer, i.e. aluminium polyphosphate layer, is covered with a silver carrier layer consisting of aluminium hydroxide with an addition of silicon hydroxide. During baking, Al_2O_3 and SiO_2 are obtained, which form an appropriate layer of the catalytic carrier. This layer is applied using the sol-gel method with a hydrolysed solution of $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$ subject to hydrolysis.

4. The assessment of surface topography of the Al_2O_3-SiO_2 carrier

The visualization of the surface topography of the Al_2O_3-SiO_2 carrier was performed using the LEO 1530 microscope equipped with the EDX microanalysis system. For microscopic tests, carrier samples were prepared on 5×10 mm plates, the surface of which was covered with a layer of carbon with the thickness of ~ 25 nm in the PVD machine at a pressure of 10^{-5} TR. 500× magnified and 5,000×magnified surface images were obtained, as presented in Figure 1.

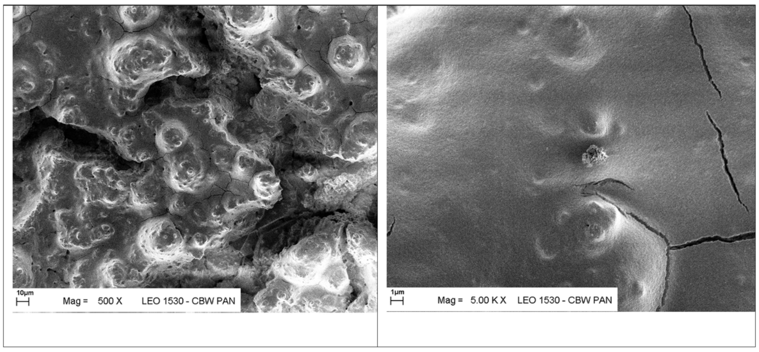

Fig. 1. SEM images of a fragment of the catalytic carrier surface Al_2O_3-SIO_2 magnified 500× and 5,000× prepared for copper impregnation

5. Acidity tests of the surface of the Al_2O_3-SiO_2 carrier

Literature review suggests a direct link between the catalytic activity in the reduction of nitrogen oxides and the acidic properties of the active catalyst carrier surface [12]. Since the results of tests of the Al_2O_3-SiO_2 carrier clearly indicate its activity in the conversion of nitrogen oxides, tests were performed to determine the acidity of the surface of the Al_2O_3-SiO_2 carrier used for the construction of Cu/Al_2O_3-SiO_2, Ag/Al_2O_3-SiO_2 and Au/Al_2O_3-SiO_2 reactors.

The acidity of the catalyst carrier surface in the form of powder isolated from the plate of the reactor model was determined using Shimadzu GCMS-QP2020 gas chromatograph equipped with a TCD concentration detector. Argon was used as carrier gas. Ammonia vapours were dosed until the ammonia peak appeared, then the sample was heated at a temperature of approx. 100ºC until the signal coming from ammonia disappeared and the ammonia desorption was started:

- 3 minutes at a temperature of approx. 100°C (373K),
- sample heating at a rate of 12 degrees/min. to approx. 420°C (693K),
- sample warm-up for 30 minutes until the ammonia signal disappeared.

The surface area between the desorption peak curve and the zero line was calculated and compared with the surface area of the test, where 4 cm^3 of ammonia became fully adsorbed on the strong centres of the carrier.

The calculation of the amount of adsorbed ammonia and surface area of the NH_3-covered carrier calculated according to the BET model (one particle may be adsorbed on one acidic centre of the catalyst), which may be a measure of the acidity of its surface, has been presented in Table 1. These calculations were performed for two temperature ranges: 373K–693K, and 600K–693K.

The results of the determinations included in Table 1 show that the developed carrier features high surface acidity. The concentrations of acid centres for aluminosilicates amount to approx. 1.012–1.014 centres per 1 cm^2, which corresponds from 0.2 to 20% of the catalyst surface occupation. The developed carrier, within the range of temperature relevant for the conversion of NO_x, has a surface covered with NH_3 which is approximately 8% greater than the acid surface present in aluminosilicates [12].

6. Tests of the specific surface and porosity of the Al_2O_3-SiO_2 carrier

The measurements of the BET specific surface of the Al_2O_3-SiO_2 catalytic carrier in the form of powder isolated from the metal plate of the reactor model were performed based on the nitrogen adsorption isotherm equation using an ASAP 2420 Micromeritics Inc. USA apparatus. The measured surface value was 195.4 m^2/g.

The volume and surface tests of mesopores in the range of their dimensions from 1.7 to 23 nm were carried out using the method developed by Barrett, Joyner and Halenda (BJH) [11].

The relationship between the steam pressure above the curved surface with the radius of curvature r_k and the steam pressure above the flat surface p_o is described by the Thomson-Kelvin equation used in the BJH method:

$$\ln\frac{p}{p_o}=\left(\frac{-2V_m}{r_kRT}\right)\cdot\cos \qquad (1)$$

where:

p – steam pressure above the flat surface [Pa],
p_o – steam pressure above the curved (cylindrical) surface [Pa],
δ – liquid surface tension [N/m],
V_m – molar volume [m^3/mol],
φ – liquid meniscus wetting angle in relation to the capillary walls [º],
R – universal gas constant [J/(mol · K)],
T – absolute temperature [K].

The phenomenon of capillary condensation is used to quantify mesoporous solids. This phenomenon occurs in transition pores (mes-

Table 1. Results of acidity determinations of the catalyst carrier surface

NH_3 desorption temperature range [K]	Dose of ammonia [mmol NH_3/g]	Number of particles [NH_3/g]	Number of particles of the [NH_3/cm^2]	Surface catalyst coated with NH_3 [%]
372–692 K	0.56	3.373×10^{20}	1.449×10^{14}	27.7
600–692 K	0.28	1.687×10^{20}	0.7245×10^{14}	13.85

opores), the diameter of which according to IUPAC classification ranges from 2 to 50 nm.

The results of the measurements of nitrogen adsorption and desorption of the total area of the mesopores and their increment using the BJH method have been presented in Figure 2, whereas the total volume and volume increment of the mesopores have been presented in Figure 3.

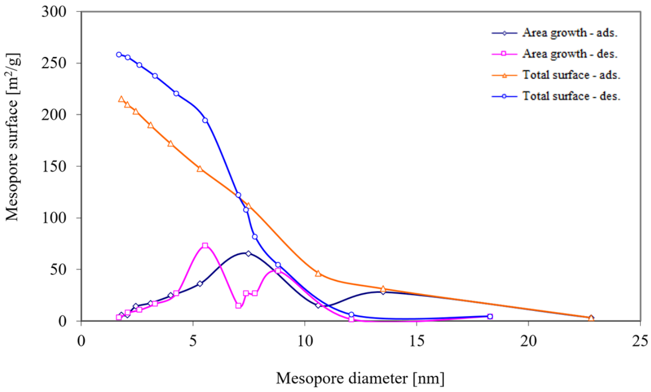

Fig. 2. The total surface area of mesopores and the increment of the mesopore surface area as a function of their diameters calculated using the BJH method with nitrogen adsorption and desorption isotherms

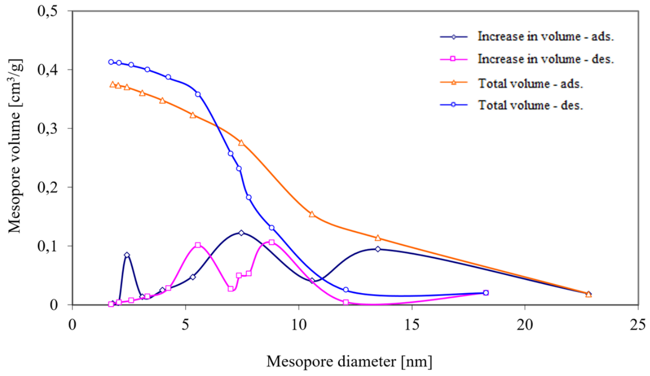

Fig. 3. The total volume of mesopores and the increment of mesopore volume as a function of their diameters calculated using the BJH method with nitrogen adsorption and desorption isotherms

7. Impregnation of the carrier with selected Group 11 elements

After drying and baking, the monoliths were covered with copper, silver and gold using the carrier impregnation materials listed in Table 2. As a result, research reactors were obtained, which were characterized in Table 2.

Table 2. Reactor characteristics

Reactor	Metal content [g/dm^3]	Materials used for carrier impregnation
Cu/Al_2O_3-SiO_2	4	Copper nitrate $[Cu(NO_3)_2 \cdot 3H_2O]$
Ag/Al_2O_3-SiO_2	4	Silver nitrate, formic acid
Au/Al_2O_3-SiO_2	4	Chloroauric acid

8. Tests of NO_2, NO, and C_3H_6 conversion as well as CO and N_2O formation

The research catalytic reactors were placed in an electric furnace and the actual exhaust fumes from a diesel engine with direct injection were passed through them at a constant relative volume flow rate SV = 30,000 h^{-1}. Directly downstream the engine outlet header, propylene was added to the exhaust fumes at a constant dose of approx. 800 ppm. The reducing agent dose was measured using a rotameter. The engine was supplied with commercial diesel fuel manufactured by PKN Orlen with a sulphur content of up to 10 ppm. The exhaust fumes temperature was measured upstream and downstream of the catalytic reactor, and the average value of the measured temperature was adopted as the catalytic reaction temperature. Gas concentration was measured using the AVL CEB2 analyser using the following techniques. The concentrations of NO and NO_2 were measured using the CL method, the concentrations of C_3H_6 were measured using the FID method, the concentrations of N_2O, CO and CO_2 were measured using the IR method, and the concentrations of O_2 were measured using the paramagnetic method. The measurements were performed until reaching the average exhaust fumes temperature $T_s \sim 600$ C°. Based on the results of the measurements, the following parameters of changes of exhaust fumes components in the reactor models were determined:

$$\text{Conversion of } NO_2\text{, NO and } C_3H_6 \quad k_i = \frac{C_{ip} - C_{iz}}{C_{iz}} \cdot 100\% \tag{2}$$

$$\text{Formation of } N_2O \text{ and CO} \quad p_i = \frac{C_{iz} - C_{ip}}{C_{iz}} \cdot 100\% \tag{3}$$

where:

C_{ip} – concentration of the i-th component upstream the reactor,
C_{iz} – concentration of the i-th component downstream the reactor.

A comparison of test results for the developed models of reactors depending on the catalytic reaction temperature with the constant addition of propylene has been presented in figures 4–8.

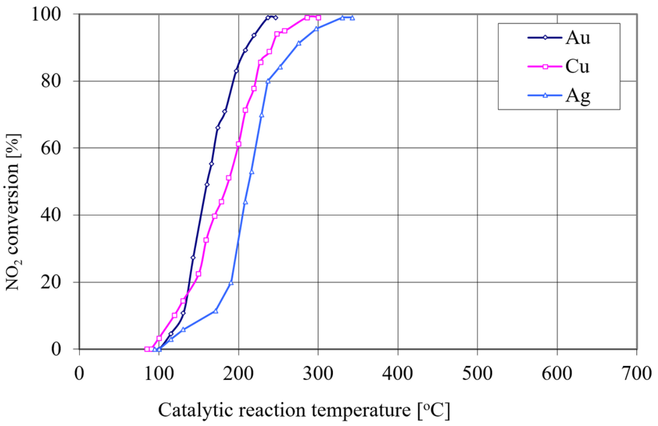

Fig. 4. The conversion of nitrogen dioxide depending on the temperature of catalytic processes for researched models of reactors upon NO_X reduction with propylene upon mixture combustion with the composition λ = 4.1. Initial concentrations of exhaust fumes components were as follows: NO_2 = 70÷100 ppm, NO = 365÷420 ppm, N_2O = 85÷100 ppm, C_3H_6 = 810÷830 ppm, CO = 0.04%, CO_2 = 5%, O_2 = 13.7÷13.9%. Relative volumetric exhaust fumes flow rate SV = 30,000 h^{-}

9. Analysis of test results

The properties of developed models of reactors were evaluated based on the determined conversion parameters and the formation of exhaust fumes components. The basic criterion was the conversion of nitric oxide, nitrogen dioxide and hydrocarbons. The reactor evaluation also took into account the secondary effects of the selective reduction of nitrogen oxides, such as the formation of additional amounts of nitrous oxide and carbon monoxide.

Conversion of NO and NO_2 and C_3H_6

The parameters of gas conversion in the tested reactor models, such as k_{max} – the maximum achieved conversion, and T_{50} – 50% conversion temperature have been presented in Table 3.

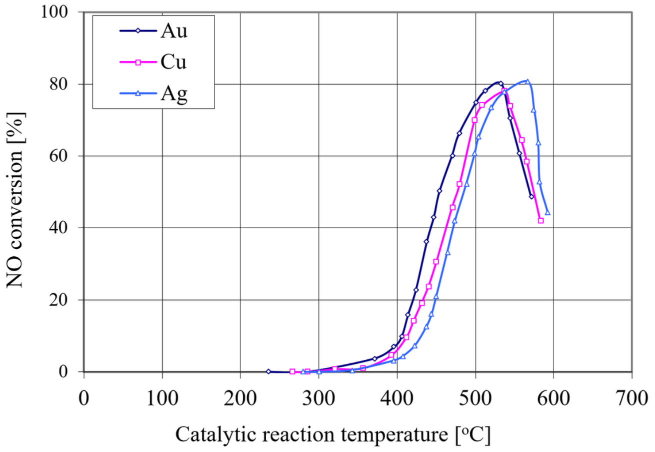

Fig. 5. The conversion of nitric oxide depending on the temperature of catalytic processes for researched models of reactors upon NO_X reduction with propylene. Initial concentrations of exhaust fumes components as shown in Fig. 4

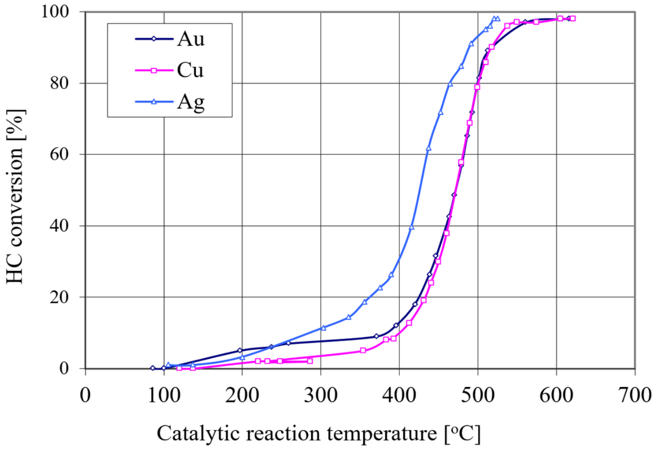

Fig. 6. The conversion of hydrocarbons depending on the temperature of catalytic processes for researched models of reactors with NO_X reduction with propylene. Initial concentrations of exhaust fumes components were as shown in Fig. 4

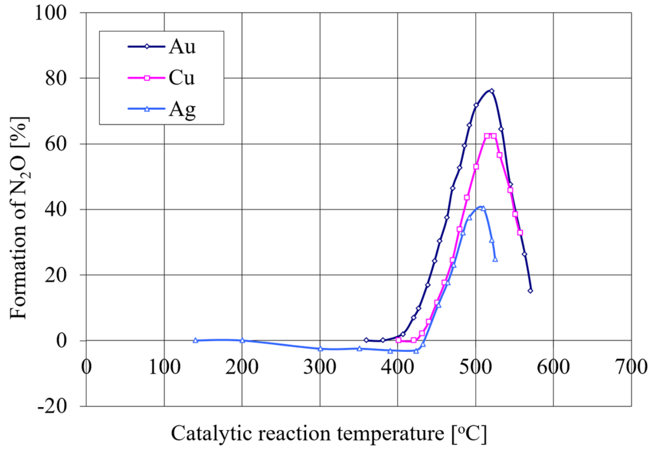

Fig. 7. The formation of nitrous oxide depending on the temperature of catalytic processes for tested reactor models upon NO_X reduction with propylene. Initial concentrations of exhaust fumes components as shown in Fig. 4

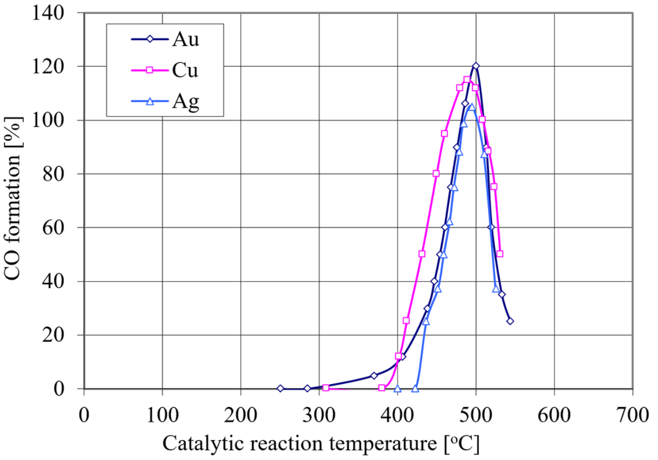

Fig. 8. The formation of carbon monoxide depending on the catalytic process temperature for the tested reactor models upon NO_X reduction with propylene. Initial concentrations of exhaust fumes components were as shown in Fig. 4

Table 3. Conversion parameters of NO, NO_2 and C_3H_6

Reactor	Conversion parameters					
	NO_2		NO		C_3H_6	
	k_{max} [%]	T_{50} [°C]	k_{max} [%]	T_{50} [°C]	k_{max} [%]	T_{50} [°C]
Au	99	160	80	455	98	
Cu	99	180	78	475	98	
Ag	99	210	81	480	98	

The developed reactors have similar NO, NO_2 and C_3H_6 conversion properties. They achieve almost 100% NO_2 conversion at a relatively low temperature (160–210°C) and NO conversion of up to 80% at relatively high temperature (455–480°C) as well as C_3H_6 conversion of approximately 98%.

The most prospective was the A reactor, obtaining relatively large NO conversion at the lowest temperature.

Formation of N_2O and CO

Parameters of gas formation in the tested catalysts, such as p_{max} – maximum formation and T_{50} – temperature of formation of 50% have been presented in Table 4.

A characteristic feature of the developed reactor models is the formation of nitrous oxide as an intermediate product of NO reduction, reaching 80% for Au and Cu catalysts. In this case, the Ag reactor displays the best properties, forming only approximately 40% of N_2O. The developed reactors also generate large amounts of carbon monoxide (above 100%) as an intermediate product of hydrocarbon oxidation.

Table 4. Parameters of N_2O and CO formation

Reactor	Formation parameters			
	N_2O		CO	
	p_{max} [%]	T_{50} [°C]	p_{max} [%]	T_{50} [°C]
Au	76	475	120	455
Cu	62	495	115	430
Ag	41	-	105	460

10. Conclusions

The developed models of reactors using Group 11 elements (Au, Cu and Ag) do not meet the conditions enabling their use in NOx reduction with hydrocarbons as independent reactors in the actual combustion engine. They achieve high NO conversion at temperatures above 450°C, reaching 80% at 550°C. Unfortunately, they do not achieve sufficiently high NO_X conversion over the full exhaust fumes temperature range (200–500°C) of the diesel engine and will result in high hydrocarbon emissions (below 500°C) and high carbon monoxide emissions (around 500°C) as well as nitrous oxide. An analysis of available literature on the use of silver in the amount of 4% by weight of the Al_2O_3 carrier in the HC-SCR catalyst indicates that the use of light alcohols (ethanol) as a reducing agent has a positive impact [7] on increasing the conversion to 98% and reducing the T_{50} temperature to 260°C. On the other hand, a bimetal reactor with a content of 1% AG and 11% of Au in Al_2O_3 achieves [17] NO_x conversion of almost 100%. Research on the impact of copper in the form of its ions placed in ZSM5 zeolite [13] confirmed the possibility of achieving a conversion of 90% at a T_{50} temperature of 300°C. Therefore, it is necessary to conduct further research of catalytic materials, in particular systems of catalytic materials (with the use of Group 11 elements, possibly with the addition of noble metals) while reducing NO_x with alcohols which may better meet the requirements occurring in the process of catalytic exhaust fumes treatment of the diesel engine.

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