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VEHICLE EXHAUST GAS EMISSION AND ITS CATALYTIC DEPOLLUTION

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In the transport process the most dominant factor is the time factor. In the industrialized world a large part of the emission of the primary air pollutants (NO_x, volatile organic compounds (VOC) and CO) originates from road traffic. Here we present the major source of the air pollutants in the cities caused by the vehicle emissions in Hungary. Besides the growing number of vehicles and development of reducing the exhaust air pollutants of the ignition motor running conditions, the total emission is growing. The air pollution regulations and law control related to the traffic and some technical evaluations to decrease the motor air pollutants are summarised. Some experimental studies were carried out to investigate the activity of used commercial catalysts for cleaning processes of Otto engines exhaust gases. The structure of catalyst samples were characterised by morphological properties namely surface area and pore volume. On the based of experimental data we stated that the commercial catalyst activity in nitrogen-oxide reduction and methane combustion reactions decrease correlated to the running period and conditions of them.

Keywords: gas emissions, vehicle, catalytic converter, nitrogen oxides, hydrocarbons

Introduction

The sustainable development should be taken into consideration in everyday life activities, that is respected behind the process mechanization, automatization the environmental and atmosphere protection problems as well. Air pollution and its impact on human health have become issues of increasing public concern during the last decades, since the pollution prevention concept emerged many years ago [1]. After the Central European countries jointed to the European Union the environmental protection topics got key role. The next laws are regulating the quality protection of human existence insurant ambient air in this area [2]:

- Government Decree No. 306/2010 (XII. 23.), on the protection of air,
- Ministry of Country Development Decree No. 4/2011 (I. 14.), on the limits of the load level of the air and on the emission limits of the fixed air polluting sources,
- Ministry of Country Development Decree No. 5/2011 (I. 14.), about modification related to the air protection,
- Ministry of Country Development Decree No. 6/2011 (I. 14.), on the rules of the examination control and evaluation of the load level of the air and the fixed air polluting sources,
- Ministry of Environment and Water Decree No. 4/2002. (X. 7.) on the designation of air pollution agglomerations and zones,
- Ministry of Transport, Communication and Building Decree No. 6/1990. (IV.12.) on technical conditions of road vehicles issue and run.

Numbers of ignition engine vehicles are exceeding the one billion in the world mainly used for transportation purpose. The number of the cars, buses and motorcycles and trucks running on roads exceeded one billion values in 2010, and increase about 40 million per a year. The estimated number of ignition vehicles will increase to 124 million all over the world by 2015. The types and numbers of the vehicle used are varying country by county [3]. *Table 1* shows the changing of vehicular structure related to Hungary.

Until 1960's the industrial production was the major source of the air pollutants in the cities, but later the air pollution is mainly caused by motor vehicles emissions.

More than 85% of traffic-related air pollutions are coming from motor vehicles exhaust emission. In Hungary about 35–40% of air pollutants can be originated to the public traffic emission. In urban area it sometimes can reach near 90%. Number of cars and trucks were increased during last 25 years period in 2 and 2.6 times respectively in Hungary as it can be seen in *Table 2*, at the same time the number of buses decrease by about 30%. The average utilization of motor vehicle increases by year to year as the statistical data show [4].

Table 1: Number of different type of vehicles in Hungary

	1985	1990	1995	2000	2005	2010
Cars	1 435 937	1 944 553	2 245 395	2 364 706	2 888 735	2 984 063
Motorcycles	395 622	168 817	159 091	91 193	122 705	142 251
Buses	24 854	26 121	20 223	17 855	17 450	17 641
Trucks	157 136	224 061	292 144	342 007	391 731	416 672
Lurries	31 392	38 397	32 613	24 426	35 917	48 207

Table 2: Gasoline and diesel engine exhaust emission and health effect

Pollutant	**Gasoline engine**	**Diesel-engine**	**Ratio of gasoline/diesel**	**Health effect**
	g emission/ dm^3 fuel			
Carbon monoxide	350	20	17.5	non-carcinogenic
Hydrocarbons	50	39	1.28	carcinogenic
Nitrogen oxides	17	23	0.74	carcinogenic
Lead compounds	0.4	0	-	carcinogenic
Soot (particle)	1.5	8	0.2	carcinogenic
Sulphur dioxide	0.2	8	0.03	reduced lung function

In spite of improvement for the combustion system of vehicles, the emission of air pollutants increases due to of growing number and age of vehicles [5].

In case of optimal conditions the fuel and air mixture could be burnt completely resulting carbon-dioxide (CO_2) and steam. For the total combustion of the fuel an optimal air-fuel mass ratio is required, otherwise the combustion results an incomplete process producing air pollutant gases: carbon monoxide (CO), hydrocarbons (CH_x), nitrogen oxides (NO_x), polyaromatic hydrocarbons (PAH), volatile organic compounds (VOC), and increasingly growing emission of aerosols as well. Otto type and diesel engine have similar air pollutants but different concentration in the exhaust gases [6]. In case of gasolined engine the gas phase pollutant are performed while diesel engines get mainly solid particles and nitrogen oxides (NO_x) into the air. Diesel engined vehicles particle- mostly contain cracked products with an order of magnitude higher than the petrol engines. Suspended carbon (soot) presents in significant amount in diesel exhaust gases on which polycyclic hydrocarbons (e.g. 3,4-benzpyrene) are able to adsorb. These fine particles have carcinogenic effect and can lodge in lungs and cause respiratory and heart problems. Also unburned polycyclic hydrocarbons adsorb on other airborne particles present in air, therefore the environmental impact of hazardous substances depends on efficiency of engine air purification system. The sulphur oxides can be detected in exhaust gases of diesel engines due to the presence of decreasing sulphur in diesel fuel.

Table 2 shows the difference between gasoline- and diesel engines exhaust emission.

Lead emission is decreased significantly for last decade, because leaded fuel was withdrawn from allowed commercialized fuels since April 1st, 1999. SO_2 emission is stepwise decreasing, due to constantly development and improvement of fuel processing technology.

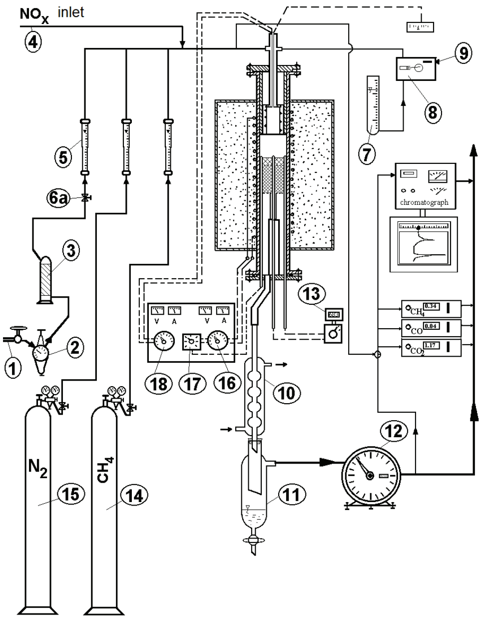
The main possibilities to reduce the vehicle exhaust gas emission are the follows [7]:

- development of vehicle with lower fuel consumption by:
  - decrease of rolling friction by 25% causes 4%
  - decrease of aerodynamic resistance by 25% causes 6%
  - decrease of mass of vehicle (e.g.: vehicle part made from plastic and aluminium) by 25% leads to decrease consumption of fuel by 17%.
- introduction traffic control measures and arrangements
  - traffic telemetry
  - green wave organization, building ring roads, roads with slow lines
- Policy and legal arrangements and laws:
  - prohibit of using vehicle above 3.5 tons from rural area
  - official emission control document
  - updating and implementation of new normative (EURO normative)
- change the type of fuel (e.g. liquefied petroleum gas, biodiesel)
- development and improvement of engine construction
- exhaust gas purification
- use of alternate fuel (e.g. hydrogen, bioethanol, biodiesel)

Experimental method

The catalytic tail gas purification methods to clean of Otto engines exhaust gases are widely applied in the practice. These three-way catalysts are known to suit requirements of EURO VI normative during the running period. The aim of experimental studies to get measured data about the activity of the commercial catalysts samples collected after different time of period and running conditions. The catalytic transformation efficiencies of methane and nitrogen oxide were used to characterize the activity of examined catalyst samples. For testing the catalyst samples a measuring system was constructed as it is shown on *Fig. 1.*

The main part of the measuring device is a tubular flow reactor with 44 mm in inner diameter. A 44 mm diameter, 50 mm long cylinder-shaped segments was cut out from catalyst samples for the studies. Two thermocouples -moveable in axis in wells- are placed into the reactor to determine the radial and axial temperature profile of the catalyst bed. After loading the catalyst samples into the tube, the test reactor body was heated up and operated in controlled conditions (heating rate, gas flow rate and composition) applying different flow rate of natural gas in the inlet gas mixture as a model exhaust gas (these measurements were carried out with gas mixture containing methane; methane and in constant flow rate of steam; methane, constant flow rate of steam and nitrogen oxides). The carbon monoxide-, carbon dioxide-, methane-, oxygen- and hydrogen concentration in the outlet gas of catalytic test reactor were determined. The carbon monoxide, carbon dioxide and methane concentration were detected by on-line NDIR (Non Dispersive Infrared) analysers (Servomex 1490), while the oxygen, hydrogen, over measuring range of methane and carbon monoxide concentration were detected with Chromatron GCHF-18-3 type gas-chromatograph using 5A type molecular sieve packed column and thermal conductivity detector. The concentration of nitrogen oxides were analysed with chemiluminescence NO-NO_x analyser (Thermo Environnement Inc., type Model 42-H). The methane flow rates of the model gas mixture were adjusted according to molar ratios of the oxidant components (the gas flow contained nitrogen oxide were produced by catalytic oxidation of ammonia in controlled conditions). The composition of the inlet gas mixture was characterised by the so called air excess factor [λ] (the ratio of the stoichiometric and applied amount of the reductant medium in practice). Origin, properties and main parameters of the catalyst samples used are collected in the *Table 3.*



1 natural gas inlet
2 pneumatic air flow controller
3 desulphurization unit
4 inlet NO_x flow control
5 rotameter
6 natural gas flow control valve
7 water measuring cylinder
8 water pump
9 water flow controller
10 water cooler
11 condensate storage
12 wet gas-meter
13 digital temperature reading unit
14, **15** gas cylinders
16, **18** toroid transformator
17 temperature controller

Figure 1: For catalyst samples testing analysis constructed measuring system

Table 3: The used catalysts samples

Catalyst sample	Description
A	Almost new (shattered): ~5000 km running, mechanically damaged, taken out from exhaust pipeline
B	Used (shattered): after 30000 km running, mechanically damaged, taken out from exhaust system
C	Used (exchanged): replaced after environmental control, without mechanical damage
D	Used (partly melted): replaced after the engine control, breakage pieces

The specific surface area and pore size distribution in the micropore (0–2 nm), mesopore (2–50 nm), and the macropore (50–300 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2000-type instrument on samples previously out gassed overnight in vacuum at the temperature of 100 °C. The surface areas of the samples (S_{BET}) were determined by the BET method from the corresponding nitrogen adsorption isotherm [8]. The meso and macropore volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) theory [9]. The pore volume of pores have 10–15000 nm in diameter range were determined by mercury penetration method using Carlo Erba Porozimetro'70 device.

Results

The activity tests of the samples were carried out in laboratory scale equipment introduced in Fig. 1.

Fig. 2 shows the methane conversion over „new” type of A catalyst. Nitrogen oxides reduction conversion over this catalyst is showed on *Fig. 3.*

The activity of applied catalyst for depollution process significantly depends on operation temperature. *Fig. 4* display the methane and nitrogen oxides conversion over A type catalyst at 600 and 700 °C temperature and at different stoichiometric ratio, λ.

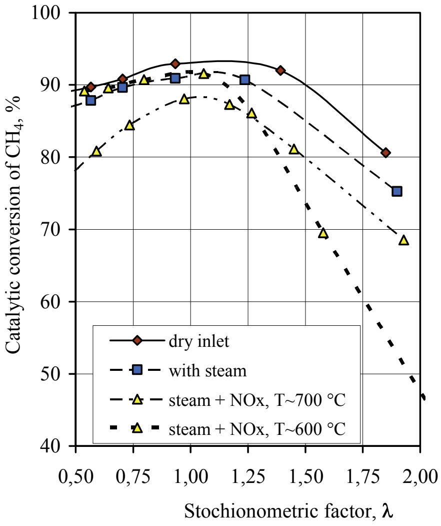


Figure 2: Methane oxidation efficiency

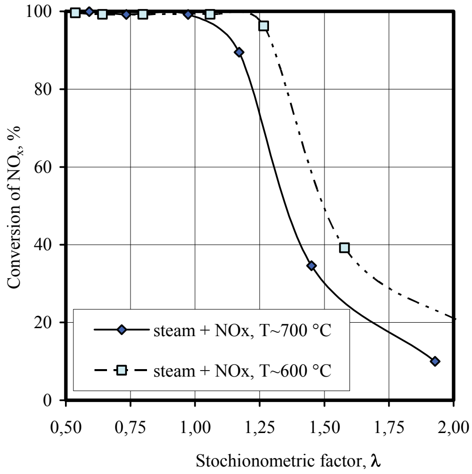


Figure 3: Nitrogen oxides oxidation efficiency

Comparison of activity of catalysts used for different periods of time is shown in *Fig. 5* and *6* It can be observed that activity of methane combustion and nitrogen oxides reduction decreases with increasing of running time period of catalysts, especially for the used catalyst sample D.

Changes in morphological structures of catalysts used for different circumstances observed are summarized in *Table 4.* (BET surface area: S_{BET}, m^2/g, mesopore-volume: $V_{1.7\text{-}300\ nm}$, cm^3/g, surface macropore, calculated from result of mercury penetration measurements: S_{BJH} m^2/g and macropore-volume: $V_{10\text{-}15000\ nm}$, cm^3/g).

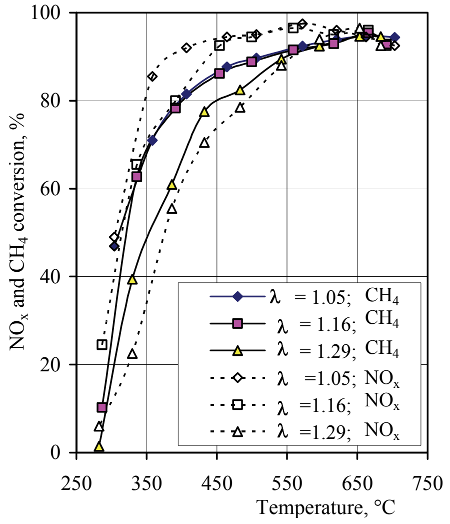


Figure 4: Methane and nitrogen oxides conversion over A type catalyst

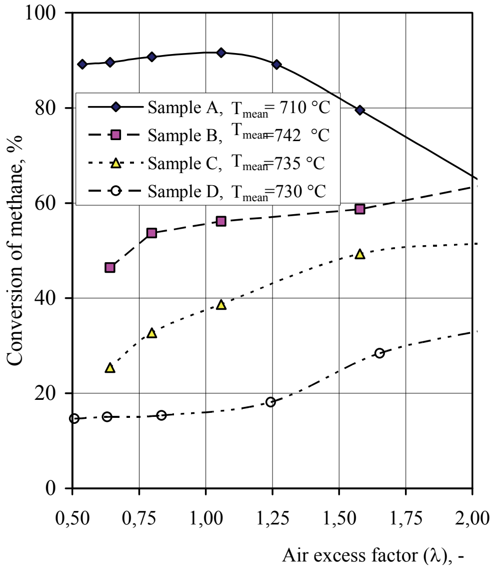


Figure 5: Methane conversion over catalysts

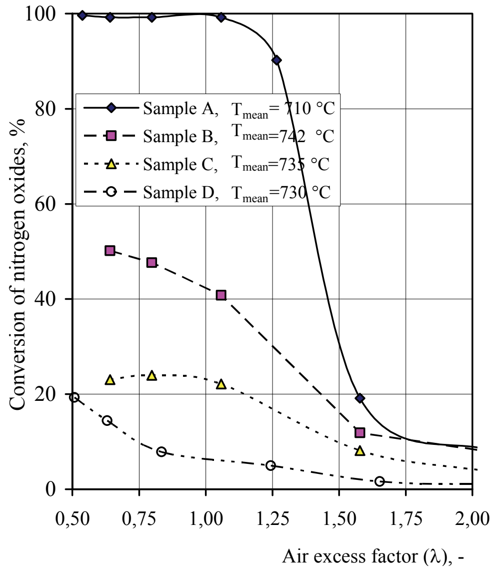


Figure 6: Nitrogen oxides reduction over catalysts

Table 4: Morphological structures of catalysts

Sample	S_{BET}, m^2/g	$V_{1,7\text{-}300\ nm}$, cm^3/g	S_{Hg}, m^2/g	$V_{10\text{-}15000\ nm}$, cm^3/g
A	5.47	0.0381	3.41	0.231
B	2.78	0.0202	1.51	0.187
C	1.86	0.0144	0.89	0.151
D	0.14	0.0007	0.77	0.142

Conclusions

The utilization period of motor vehicle, engine construction and technical conditions of the catalysts significantly influence the exhaust emission level of the internal combustion engine. Increasing the operation time of catalysts the catalytic activity of hydrocarbon oxidation and nitrogen-oxide reduction decreased which might be directly associated with changes in catalyst morphological structure.

At least the operating temperature and conditions of the catalyst should be continuously controlled during the operation of the catalyst in the engine exhaust gas system.

For these reason the tests on the catalyst structure and activity of the new catalysts after thermal shock under controlled conditions are in progress.

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