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CATALYTIC OXIDATION OF ORGANIC COMPOUNDS INCLUDING POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM MOTOR EXHAUST GASES

A major contribution to the PAHs emission in the urban areas comes from motor exhaust gases emitted by both spark ignition and Diesel engines. Catalytic converters are widely used devices for the spark ignition emission control. A monolithic noble metal catalyst (Pt, Pd, Rh) was manufactured for the purpose of the study. Its activity was tested in the oxidation of volatile organic compounds (VOCs) and PAHs emitted with real exhaust gases from one-cylinder spark ignition engine. The efficiency of VOCs catalytic oxidation varied depending on the engine load and air/fuel ratio. Under "lean-burn" conditions (regulated engine work) PAHs were oxidized almost completely; only naphtalene in trace concentration was detected in the off-gases. When the motor worked without regulation, at deficit of oxygen, soot was generated. Under such conditions the catalyst was partially blocked in with soot and deactivated. After engine regulation, catalyst regenerated itself and regained its original, high activity.

1. INTRODUCTION

Motor exhaust gases are one of the major sources of air pollution in the urban area. In exhaust gases, both from spark ignition and Diesel engines, there are emitted carbon monoxide and nitrogen oxides as well as organic compounds: volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and their oxy- and nitrogen derivatives. PAHs and their derivatives are one of the first atmospheric pollutants identified and there were reasons to suspect that they could be cancerogens and mutagens. Generally, Diesel motors produced smaller quantities of regulated gaseous emissions, namely CO and unburned hydrocarbons, than do similarly powered petrol engines [1].

The emission rates of organic compounds, particularly PAHs, from motor vehicles are known to be dependent on a number of factors including engine type, driving con-

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ditions such as engine load, air/fuel ratio and cold start behaviour as well as fuel composition. Fuel aromaticity, PAHs accumulation in lubricant oil and lubricant oil combustion also influence the emission rates of PAHs. The exact mechanism of PAHs formation during combustion is not understood in detail. Because the combustion process within the internal combustion engine has to occur very rapidly, the radical formation mechanism is considered to be favoured. Comparison of individual PAH patterns in the vehicle fuels with those in the ambient air of traffic source showed that a significant fraction of PAHs was formed during incomplete combustion with thermal synthesis. In high-traffic areas, concentration of benzo(a)pyrene (BaP) was found to be significantly correlated with CO concentration; both of them are typical products of incomplete oxidation [2]–[5].

Catalytic conversion of air pollutants (over oxidative or three-way catalysts) is actually the most efficient method of emission control of gasoline fueled vehicles. ROGGE et al. [6] report that noncatalyst vehicles show the highest emission rates for each of the PAH detected; a more than 25-fold higher total PAH emission rate is observed for autos without catalytic converters than for autos equipped with catalytic exhaust emission control devices [6].

The Research Group of Environmental Catalysis at the Wrocław University of Technology has been working for many years on the preparation, manufacture and application of catalysts to the combustion of organic air pollutants, particularly from industrial flue gases. Recently, a new type of a monolithic catalyst on cordierite or metal foil support was manufactured. It was interesting to test this catalyst activity in the oxidation of organic air pollutants, including PAHs emitted in motor exhaust gases.

For the purpose of the study, the catalyst P-2 was prepared on a cordierite monolithic support. Its catalytic activity was tested at regular engine work (lean-burn conditions) and at deficit of oxygen (simulation of inadequate conditions of engine work), which produced soot observed in the exhaust gases.

2. MATERIALS AND METHODS

Noble metal catalyst on cordierite support was manufactured for the purpose of the study. A cordierite monolith was impregnated with a colloidal solution of aluminium hydroxide with thermal stabilizers – rare earth elements and titania. As it was found earlier, these additives enable easier autoregeneration of the catalyst partially blocked by soot particles. After drying and calcinating the γ-Al_2O_3 washcoat content accounted for ca. 2 mass % of the cordierite support. Active ingredients were deposited on the washcoat by immersion in the solution of chloroplatinic acid, palladium chloride and rhodium chloride.

The parameters of the catalyst are listed below:

cell shape – square,
cell density – $32/cm^2$,
cell dimension – 1.45 mm,
wall thickness – 0.35 mm,
open area – 64%,
active ingredient – Pt (0.07 mass%), Pd (0.04 mass%), Rh (0.016 mass%),
monolith dimension – $h = 74$ mm, $\phi = 94$ mm.

Investigations were carried out on real exhaust gases emitted from a one-cylinder spark ignition engine S 101, fueled with commercial lead-free gasoline E-95:

• at three engine loadings (changed by an electric stove): idle run, 30% (500 W) and 60% (1000 W);

• at a constant engine rotation – 2800 rev/min;

• at two engine work conditions – the regular engine work (lean-burn conditions) and fuel combustion with deficit of oxygen.

Activity of the catalyst was tested in the reaction of detected VOCs and selected PAHs oxidation.

3. SAMPLING AND ANALYSIS OF ORGANIC AIR POLLUTANTS IN THE EXHAUST GASES

Volatile organic compounds were collected in polyethylene sampling bags, concentrated on activated carbon, desorbed with CS_2 during 30 min and analysed by gas chromatography with data integrator system. Perkin Elmer GC 3920 was equipped with flame jonization detector (FID) and column (1.8 m × 2.7 mm) packed with 10% PEG on Chromosorb W. Temperature of column amounted to 73 °C, while the temperature of injector and detector reached 150 °C.

Exhaust gas samples for both particle and gas phases of PAHs were collected using a glass fibre (Staplex TFAGF 810) and a glass cartridge containing graphitized carbon sorbent (SKC-lot 120, USA). The PAHs adsorbed were extracted from whole organic matter and concentrated before gas-chromatography analysis. Method of PAHs extraction is presented in figure 1. A Hewlett-Packard GC 5890, Series II, was equipped with FID, split-splitless injection, HP-1 capillary column and a computer work station. The temperatures of injector and detector reached 260 and 280 °C, respectively. Oven temperature was programmed from 60 °C (2 min) to 270 °C at 12 deg/min, and held at 270 °C for 40 min. The GC was calibrated with a diluted standard solution of 16 PAHs (PAH-Mix IX, Dr Ehrenstorfer GmbH). The quantitative identification was accomplished using relative retention times for each compound. PAHs recovery efficiency was determined by means of binaphthyl as internal standard.
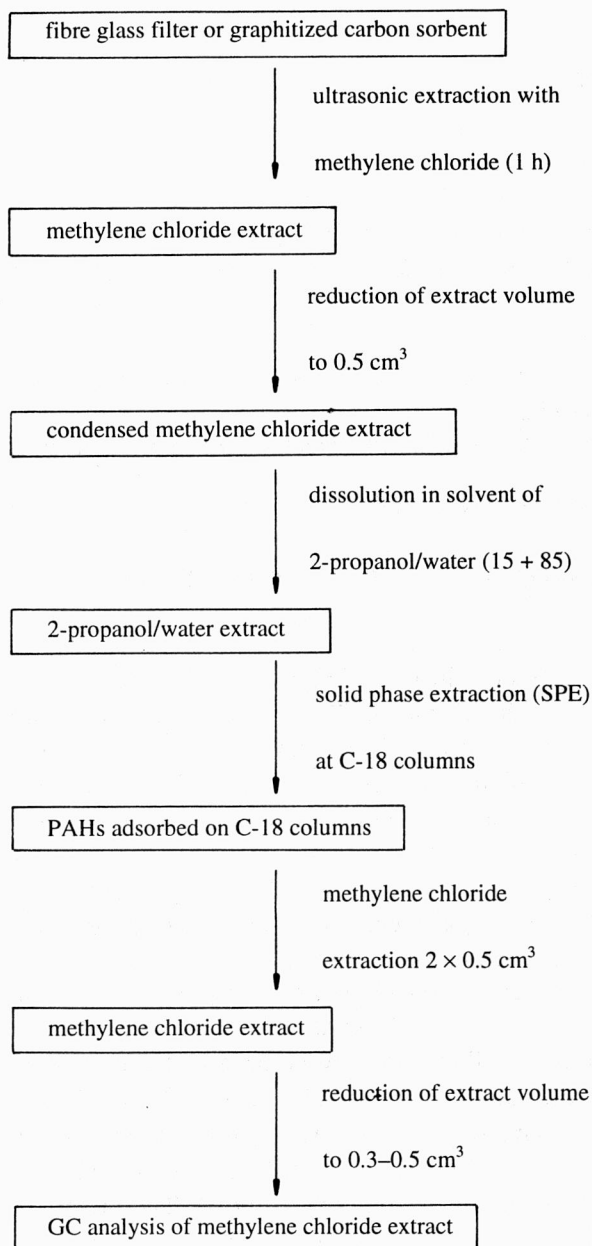
PAHs EXTRACTION

| fibre glass filter or graphitized carbon sorbent |

     ultrasonic extraction with

     methylene chloride (1 h)

| methylene chloride extract |

     reduction of extract volume

     to 0.5 cm^3

| condensed methylene chloride extract |

     dissolution in solvent of

     2-propanol/water (15 + 85)

| 2-propanol/water extract |

     solid phase extraction (SPE)

     at C-18 columns

| PAHs adsorbed on C-18 columns |

     methylene chloride

     extraction 2 × 0.5 cm^3

| methylene chloride extract |

     reduction of extract volume

     to 0.3–0.5 cm^3

| GC analysis of methylene chloride extract |

Fig. 1. PAHs extraction and concentration before gas chromatographic analysis

4. RESULTS AND DISSCUSION

Two groups of organic compounds in exhaust gases were analysed, i.e., VOCs and PAHs. Average concentrations of the VOCs detected and PAHs identified during regular engine work are presented in tables 1 and 2. Distribution of PAHs between gas and solid phases (extracted from graphitized carbon sorbent and from glass fibre filter, respectively) is presented in figure 2.

Table 1

Average VOCs concentration in exhaust gases at various engine loadings

Compound	Concentration [mg/dm^3]		
	Idle run	30% load	60% load
Acetaldehyde	0.3310	0.2080	0.1340
Butyraldehyde	n.d.	0.0086	0.0064
Acetone	0.0013	0.0120	0.0045
Acrolein	0.0020	0.0240	0.0002
Benzene	0.0527	0.0675	0.0329
Toluene	0.0208	0.0390	0.0488
Xylene	0.0015	0.0006	0.0035
Ethylbenzene	0.0011	0.0023	0.0009
Alkanes (as pentane)	0.112	0.165	0.095

Table 2

Average PAHs concentration in exhaust gases
at two engine loadings (30% and 60%)

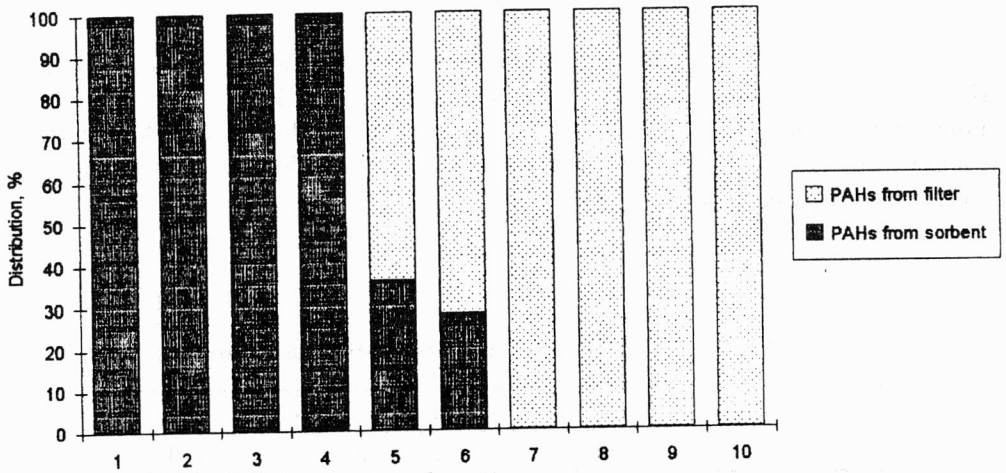| Compound	Concentration [μg/dm^3]	
	30% load	60% load
Naphtalene	12.969	13.304
Acenaphtylene	0.514	0.374
Acenaphthene	0.104	0.300
Fluorene	0.190	0.181
Anthracene	0.039	0.021
Phenanthrene	0.115	0.037
Fluoranthene	0.175	0.029
Pyrene	0.230	0.054
Benzo(a)anthracene	0.273	0.009
Chrysene	0.005	n.d.

n.d. – not detected.

Fig. 2. Distribution of analysed PAHs extracted from fibre glass filter and graphitized carbon sorbent:
1 – naphthalene, 2 – acenaphthylene, 3 – acenaphthene, 4 – fluorene, 5 – anthracene,
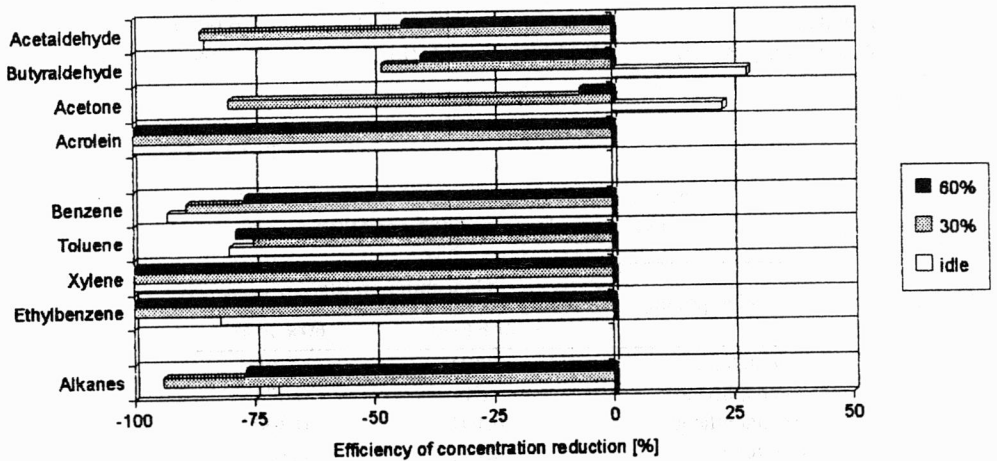6 – phenanthrene, 7 – fluoranthene, 8 – pyrene, 9 – benzo-(a)anthracene, 10 – chrysene

Fig. 3. Efficiency of concentration reduction of selected VOCs in the off-gases
over fresh catalyst under various engine work conditions

Irrespective of engine loading, oxyderivatives occurred in high concentrations,
particularly acetaldehyde, a typical product of incomplete oxidation of various or-
ganic compounds. Acetaldehyde concentration was particularly high at the idle run of

engine, and reached 0.33 mg/dm^3. Alkanes and aromatics were presented in lower concentrations, ranging from 0.095 to 0.165 mg/dm^3, and from 0.075 to 0.11 mg/dm^3, respectively. The concentration of PAHs in the exhaust was much lower than that of VOCs. In that group of compounds, naphthalene was detected in the highest concentration (about 13 μg/dm^3); other PAHs were detected in the concentration lower than 0.5 μg/dm^3.

The efficiences of VOCs oxidation in the presence of a fresh catalyst at regular engine work (lean-burn conditions) are presented in figure 3.
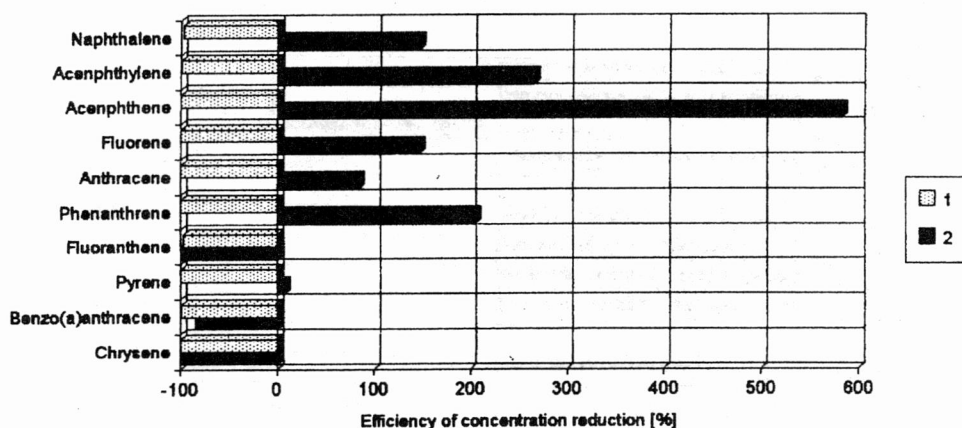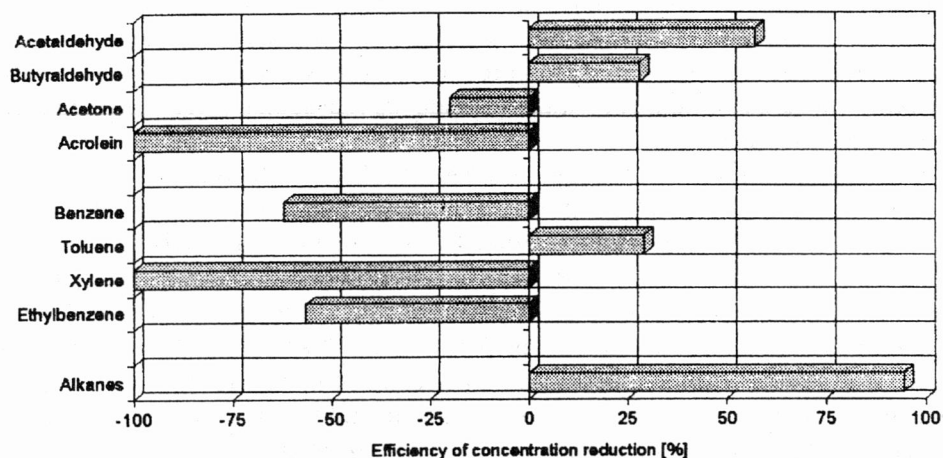

Fig. 4. Efficiency of concentration reduction of selected VOCs and PAHs
in off-gases over catalyst partially blocked in with soot (2) after engine work at deficit of oxygen;
(1) – PAHs conversion over fresh catalyst

The efficiency of particular VOCs diminution changed widely, depending on the engine load. The highest catalyst activity was observed at the engine load of 30%, and varied from 47–100%, depending on the oxidized compound. At the idle run, the concentration of butyraldehyde and acetone in off-gases was about 25% higher than that before passing over the catalyst. These compounds can also be yielded as products of incomplete oxidation of the other organic compounds. Under these conditions nearly all the PAHs were oxidized completely, except naphthalene which was combusted with 97% efficiency (figure 4).

When the engine worked without regulation, at deficit of oxygen, simulating an inadequate condition of fuel combusion, soot was produced and observed in the exhaust gases. Under such conditions soot was adsorbed on the active centres of the catalyst, thus decreasing its activity (figure 4). In exhaust gases, after their passing over catalyst, the concentrations of some compounds (particularly those of the PAHs) were much higher than those before passing over catalyst when the engine worked under lean-burn conditions. Only aromatics were oxidized with about 30% efficiency. Increased concentrations of aldehydes, organic acids and some PAHs after passing through catalytic convertors were reported by investigators of catalytic control of exhaust from wood-cutting saws or Renault cars [7], [8]. On the other hand, particles emitted in the exhaust gases produced by a spark ignition engine consist mainly of black carbon and organic compounds. The particles are of shell model, with species of low volatility adsorbed on a spherical carbonaceous core (diameter ca. 15 mm) and covered with highly volatile species. At rising temperature of combustion at regular engine run, at first the volatile compounds desorb from particle surface, and next desorption or pyrolysis of uncovered PAHs can occur, so their concentrations in the outlet gases can exceed those stated before passing the gases over the catalyst [9].
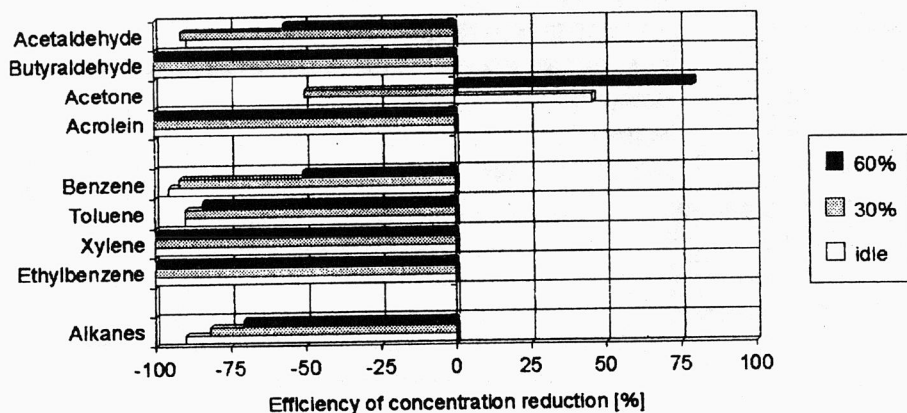

Fig. 5. Efficiency of concetration reduction of selected VOCs in off-gases
over catalyst regenerated in hot air flow (600 °C)

Reregulation of engine work (lean-burn) resulted in the autoregeneration of the catalyst (figure 6). Activity of the catalyst in the VOCs oxidation was almost completely recovered after its regeneration in the hot air flow (600 °C) during 6 hours (figure 5).
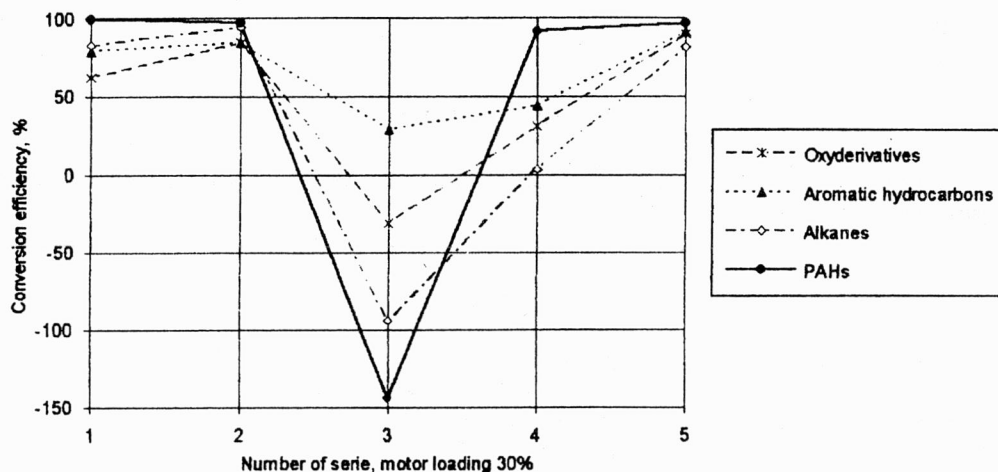

Fig. 6. Conversion efficiency of selected VOCs and PAHs over catalyst
under various engine work conditions (motor loading of 30%):
1 – cold start, 2 – lean-burn conditions – fresh catalyst, 3 – catalyst partially blocked in with soot,
4 – catalyst after autoregeneration (lean-burn condition), 5 – catalyst after regeneration in hot air

Also nearly all PAHs were oxidized completely; only naphthalene, acenaphthylene and fluoranthene were oxidized with 97% efficiency.

4. CONCLUSIONS

1. Catalyst activity in the oxidation of the VOCs depends on the engine work conditions. The efficiency of VOCs oxidation was lower under cold-start conditions (60–75%) than at regular work under lean-burn conditions (75–90%). Hydrocarbons were oxidized with higher efficiency than oxyderivatives. Higher concentrations of the oxyderivatives in the off-gases can result not only from lower catalyst activity during their oxidation, but also they can be the intermediate products of incomplete hydrocarbon oxidation.

2. In lean-burn condition, PAHs are oxidized almost completely, irrespective of the engine load.

3. Irregular motor work (fuel combusion with deficit of oxygen) results in soot formation. The catalyst is blocked in with soot and partially deactivated. Under such

conditions, the concentrations of some VOCs and PAHs in the off-gases exceed those before passing over the catalyst. Regular work under lean-burn conditions accounts for catalyst autoregeneration, partially in VOCs oxidation, and near completely in PAHs oxidation.

4. Catalyst regeneration in hot air flow (600 °C) leads to the recovery of its initial activity.

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KATALITYCZNE UTLENIANIE ORGANICZNYCH ZANIECZYSZCZEŃ POWIETRZA
WRAZ Z WIELOPIERŚCIENIOWYMI WĘGLOWODORAMI AROMATYCZNYMI (WWA)
Z SILNIKOWYCH GAZÓW SPALINOWYCH

Głównym źródłem emisji WWA w atmosferze miast są spaliny silnikowe z pojazdów samochodowych – zarówno z silników iskrowych, jak i dieslowskich. Obecnie dopalacze katalityczne znajdują szerokie zastosowanie w ograniczaniu emisji zanieczyszczeń z silników iskrowych. Do badań wykonano katalizator na bazie metali szlachetnych (Pt, Pd, Rh) na nośniku monolitycznym. Jego aktywność testowano w reakcji utleniania lotnych związków organicznych oraz WWA emitowanych w spalinach jednocylindrowego silnika spalinowego. Skuteczność dopalania lotnych połączeń zależała od obciążenia silnika i stosunku powietrze/paliwo. Podczas prawidłowej pracy silnika WWA spalały się niemal całkowicie, w gazach poreakcyjnych wykrywano jedynie ślady naftalenu. W przypadku nieprawidłowej pracy silnika i niedomiaru tlenu obserwowano tworzenie się sadzy. Blokowała ona miejsca aktywne katalizatora i powodowała jego dezaktywację. Po wyregulowaniu silnika katalizator regenerował się samoczynnie, odzyskując wysoką aktywność początkową.