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## CATALYTIC OXIDATION OF ORGANIC AIR POLLUTANTS EMITTED IN INDUSTRIAL WASTE GASES AND MOTOR EXHAUST

The latest attainments of the Environmental Catalysis Research Group in the preparation of monolithic noble metal catalysts on metallic or cordierite support are presented. Their activities were tested in the oxidation of typical solvent vapour emitted from industrial plants, and volatile organic compounds and polycyclic aromatic hydrocarbons (PAHs) in motor exhaust gases. Manufactured catalysts, which are based on Pt, Pd, Rh and one perovskite catalyst, showed high activities in the oxidation of hydrocarbons, oxy-derivatives and PAHs, and lower activities in chloroorganic compounds destruction. In the presence of chlorine compounds no deactivation of catalysts was observed.

### 1. INTRODUCTION

Organic air pollutants emitted in the industrial waste gases and motor exhaust are considered as significant atmospheric pollutants due to their toxicity and their contribution to smog generation. The major sources of this emission are various branches of chemical industry, including crude oil refineries, synthetic fiber plants, pharmaceutical and food processing industry, etc.

Catalytic combustion seems to be an efficient and economical method for destruction of organic air pollutants in terms of energy savings. The process of the catalytic oxidation of chlorinated hydrocarbons proceeds under particular conditions. The catalyst, except high activity, must be also chemically resistant to chlorine compounds. Halogenated hydrocarbons can cause a reversible deactivation of noble metal catalysts, by blocking the active sites of the catalyst by chlorine compounds. When chlorinated compounds are removed from the reaction mixture, the catalyst regains its initial activity. In case of metal oxide catalyst, chlorine can react with some metals, forming volatile metal chlorides (e.g. cobalt chloride) and a number of active sites, hence the specific surface area of catalyst decrease. This deactivation is of irreversible

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character. Generally, it is assumed that only catalysts with very high platinum content (1–3 mass %) can be applied for this purpose. However, our earlier study has shown that the catalysts with a platinum content reduced to 0.1–0.15 mass % can be effectively used [1], [2]. On the other hand, the majority of organic air pollutants in urban environment come from the motor exhaust gases, both from spark ignition and Diesel engines. Catalytic oxidation is a well known, efficient and widely applied method of gasoline-fuelled automobile exhaust control [3].

The Research Group of Environmental Catalysis in collaboration with the Group of Surface Engineering and Catalysis, both from Wrocław University of Technology, have been working for many years on the preparation and application of manufactured catalysts in the oxidation of organic air pollutants. Monolithic catalysts are the new generation of the catalyst widely applied in catalytic converter for motor exhaust control. Because of the evident advantages of this shape of the catalyst, the wide use of monolithic catalysts for industrial waste gas treatment is likely to be their main domain in the near future [4], [5]. Recently, both research groups are working on preparation of a monolithic catalyst on metallic or ceramic cordierite support. As the specific surface area of such support material is very small, it is necessary to deposit a washcoat between the support and an active phase. The best material of the washcoat consists of  $\gamma$ - $\text{Al}_2\text{O}_3$  with the addition of rare earth elements, generally lanthanum, up to 10 mass % of alumina, titanium oxide or silica. The additives increase thermal and chemical stability of catalyst [6].

Recently, some new monolithic catalysts on metallic or cordierite support were manufactured. Their activities were tested in the reaction of typical organic solvent vapour oxidation, including hydrocarbons, oxy-derivatives and chlorinated hydrocarbons, as well as in the oxidation of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) emitted in motor exhaust gases. This paper contains our late attainments in this field of research.

## 2. MANUFACTURED CATALYSTS

For the purpose of the study, seven monolithic catalysts were prepared. They are based on platinum group metals, i.e. Pt, Pd, Rh, on metallic (heat-resisting steel alloy) or ceramic (cordierite) support. Their activities were compared with the activity of metal oxide catalyst on cordierite monolithic support, with  $\text{LaMnO}_3$  with addition of silver perovskite as active phase. Description of catalyst supports is presented in table 1.

The washcoat of manufactured catalysts was prepared from a colloidal aluminium hydroxide solution, with additives. After drying and calcination the washcoat included 2.5% of support mass. The active ingredients were deposited by immersion of the support in the aqueous solutions of chloroplatinic acid, palladium or rhodium chlorides. Perovskite catalyst was manufactured without the washcoat, but its active phase was deposited by repeated twice impregnation, drying and calcination of the

catalyst support in a solution of perovskite slurry. Description of manufactured catalysts is shown in table 2.

Table 1

Description of catalyst supports

Parameter	M-1, M-2, M-3, M-4	MS-1, MS-2	PER-1	P-1
Material	heat-resisting steel	heat-resisting steel	cordierite	cordierite
Shape of cell	triangle	triangle	square	square
Cells density /cm <sup>2</sup>	270	270	32	28
Cell dimension, mm	0.7	0.7	1.45	1.5
Wall thickness, mm	0.05	0.05	0.35	0.35
Block dimension, mm	$\phi = 21, h = 70$	$\phi = 94, h = 70$	$\phi = 21, h = 70$	$\phi = 94, h = 74$

Table 2

Description of manufactured catalysts

Catalyst	Washcoat	Active ingredient
M-1	$\gamma\text{-Al}_2\text{O}_3, 2.5\%$	Pt, 0.15%
M-2	$\gamma\text{-Al}_2\text{O}_3, 2.5\%$	Pd, 0.15%
M-3	$\gamma\text{-Al}_2\text{O}_3, 2.5\% + \text{SiO}_2, 2.5\%$	Pt, 0.15%
M-4	$\gamma\text{-Al}_2\text{O}_3, 2.5\% + \text{SiO}_2, 2.5\%$	Pd, 0.15%
MS-1	$\gamma\text{-Al}_2\text{O}_3, 2.5\% + \text{TiO}_2, 0.34\% + \text{lanthanides}, 0.05\%$	Pt, 0.07% + Rh, 0.17%
MS-2	$\gamma\text{-Al}_2\text{O}_3, 2.5\% + \text{TiO}_2, 0.34\% + \text{lanthanides}, 0.05\%$	Pd, 0.2%
P-1	$\gamma\text{-Al}_2\text{O}_3, 2.5\% + \text{TiO}_2, 0.34\% + \text{lanthanides}, 0.05\%$	Pt, 0.07%, Pd and Rh, 0.04%
PER-1	without	$\text{La}_{0.5}\text{Ag}_{0.5}\text{MnO}_3, 10\%$

### 3. CATALYTIC OXIDATION OF SELECTED ORGANIC COMPOUNDS

#### 3.1. METHODS

The activities of manufactured catalysts were tested in the oxidation of selected typical organic solvents, including hydrocarbons (toluene and *n*-heptane), oxyderivatives (ethanol, acetone methyl ethyl ketone, ethyl acetate) and halogenated hydrocarbons (chlorobenzene, dichloroethylene – DCE, trichloroethylene – TCE and epi-chlorohydrin). The tests were carried out in the electrically heated glass reactor of laboratory scale. Every compound was oxidized separately and then evaporated from the specially constructed glass doser and mixed with air to the desired inlet concen-

tration of  $1 \text{ g/m}^3$ . The reaction temperature varied from 200 to 500 °C. Gas space velocity was constant and reached  $10000 \text{ h}^{-1}$ . The concentrations of reagents and eventually yielded products of incomplete oxidation – light hydrocarbons and aldehydes – were analyzed using gas chromatograph (Perkin-Elmer GC 3920, with integrator, FID and column of  $1.8 \text{ m}/2.7 \text{ mm}$  packed with 10% PEG 2000 on Chromosorb W). The temperature of column reached 73 °C, while the temperature of injector and detector amounted to 100 °C.

### 3.2. CATALYST ACTIVITY IN THE OXIDATION OF SELECTED HYDROCARBONS AND OXY-DERIVATIVES

The results of the test reaction of selected hydrocarbons and derivatives oxidation over platinum M-1 and perovskite PER-1 catalysts are presented in figure 1. Both catalysts were very active in the oxidation of selected compounds, and at temperature higher than 350 °C every compound was oxidized with 90% conversion efficiency.

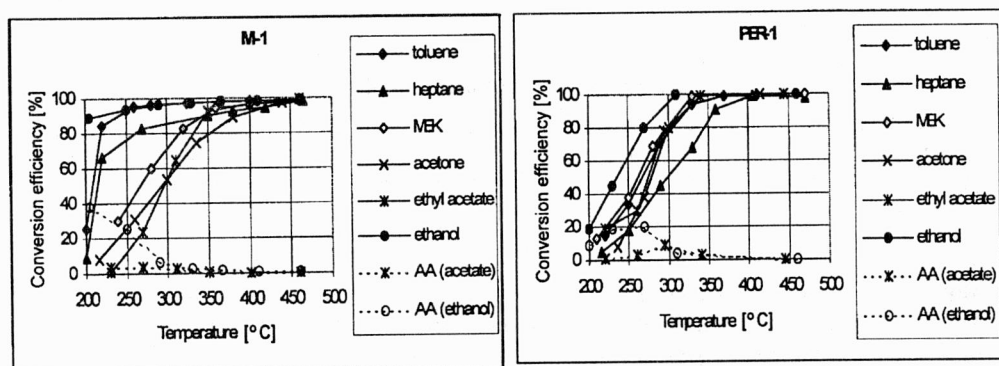


Fig. 1. Activities of platinum (M-1) and perovskite (PER-1) catalysts in selected VOCs oxidation and the concentration of the acetaldehyde (AA) yielded

Hydrocarbons were oxidized with higher efficiency in the presence of platinum catalyst, while the oxy-derivatives were oxidized similarly over both catalysts. Only when ethanol and ethyl acetate were oxidized, acetaldehyde – a typical product of incomplete oxidation – was found in the reaction gases. Our earlier study showed that in the presence of a variety of metal oxide catalysts, including perovskites, acetaldehyde was yielded during the oxidation of the other oxy-derivatives as well [7], [8]. The higher concentration of aldehyde was detected when ethanol was oxidized, and the maximum concentration in the presence of M-1 reached  $0.4 \text{ g/m}^3$  at the lowest reaction temperature of 200 °C, and  $0.2 \text{ g/m}^3$  at 250 °C over PER-1. At temperature higher than 280 and 320 °C, respectively for platinum and perovskite catalysts, only traces of aldehyde were found in the exhaust gases. Hydrocarbons and ketones were oxidized only to  $\text{CO}_2$  and water.

## 3.3. CATALYST ACTIVITY IN THE OXIDATION OF CHLORINATED HYDROCARBONS

The results of the oxidation of selected chloroorganic compounds over the platinum M-3 and palladium M-4 catalysts are shown in figure 2. Both catalysts were very active in the test reaction of toluene oxidation, and at 240 °C the conversion efficiency of toluene reached 90%. Chlorinated compounds were more resistant to catalytic reaction. Catalytic reactivity of chlorinated hydrocarbons decreased as follows:

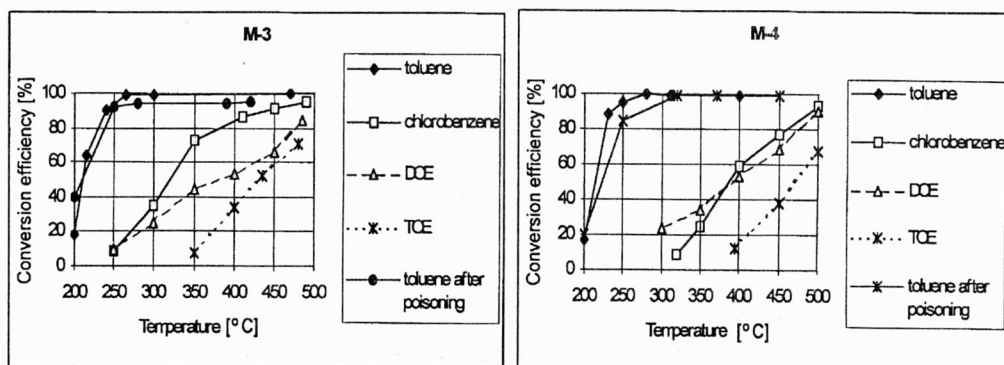


Fig. 2. Activities of platinum (M-3) and palladium (M-4) catalysts in the oxidation of selected chloroorganic compounds

The activity of the palladium catalyst M-4 in the chloroorganic compounds' oxidation was slightly lower compared with the activity of platinum catalyst, particularly when chlorobenzene was oxidized. The test reaction of toluene oxidation after all tests carried out with chlorinated compounds and after the poisoning cycle (oxidation of TCE at 450 °C during ca. 100 h) showed that the catalyst activity was nearly the same as for the fresh catalysts. Moreover, no physical changes of both contacts surfaces, e.g. attrition of active phase or washcoat, were observed. Analysis of the reaction products showed that HCl was the only chlorinated reaction product, no other chlorinated organic compounds or carbon monoxide were found in the reaction gases. Only over the platinum catalyst, under some reaction conditions, traces of chlorine were detected.

The emission of chloroorganic compounds such as epi-chlorohydrin, allyl chloride, chloropropane takes place in the process of epi-chlorohydrin production. The results of test reaction of epi-chlorohydrin oxidation, in the presence of monolithic platinum and palladium catalysts on metallic support differing in the washcoat material, are presented in figure 3. The platinum catalyst M-3 with the washcoat of  $\gamma$ -alumina with  $\text{SiO}_2$  addition was most active in this process. 90% conversion efficiency of epi-chlorohydrin was observed at 300 °C, and at the temperature higher than 350 °C epi-chlorohydrin was oxidized nearly completely. In the presence of both

catalysts under investigation, allyl chloride – the reaction by-product, was found in the reaction gases. Over M-3, the concentration of allyl chloride yielded was lower than over M-4 and maximally reached  $0.06 \text{ g/m}^3$  at  $250 \text{ }^\circ\text{C}$ . Above  $280 \text{ }^\circ\text{C}$ , no by-products were detected in the reaction gas.

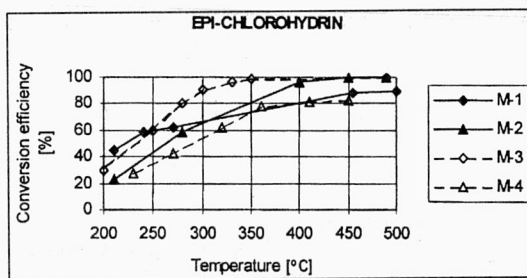


Fig. 3. Activities of platinum (M-1 and M-3) and palladium (M-2 and M-4) catalysts in epi-chlorohydrin oxidation

#### 4. CATALYTIC OXIDATION OF ORGANIC COMPOUNDS EMITTED FROM MOTOR EXHAUST GASES

##### 4.1. METHODS

The activities of MS-1, MS-2 and P-1 catalysts were tested in the oxidation of organic compounds emitted in the motor exhaust gases. The exhausts were emitted from a Briggs & Stratton one-cylinder four-stroke engine, of a capacity of  $181 \text{ cm}^3$ , fueled with the commercial lead-free gasoline E-95 and working as an electric current generator. The load of engine was changed with the electric stove. Investigation was carried out:

- at four engine load – idle run, 30, 60 and 90% engine load;
- at a constant engine rotation 2800 rev/min;
- under two engine conditions – “cold start” and after 75 minutes of the engine work.

Catalyst activity was tested in the oxidation of two group of organic compounds – volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). VOCs were collected in polyethylene sampling bags, concentrated on activated carbon, desorbed with  $\text{CS}_2$  and analyzed by gas chromatography. PAHs, both from gaseous phase and adsorbed on particles, were collected using glass-fiber filter (Staplex TFAGF 810) and glass cartridge containing graphitized carbon sorbent (SKC-lot 120, U.S.A). Before sampling exhaust gas was cooled down to ca.  $50 \text{ }^\circ\text{C}$ . Adsorbed PAHs were next extracted with methylene chloride in an ultrasonic bath and concentrated by solid phase extraction method (SPE on C-18 column with reversed octadecyl phase, of

Bakerbond system). PAHs were next analyzed by gas chromatography (Hewlett-Packard GC 5890, with FID, HP-5 capillary column of 30 m/0.53 mm, at a temperature programmed from 60 to 280 °C and computer work station). The GC was calibrated with a diluted standard solution of 16 PAHs (PAH-Mix IX, Dr. Ehrenstorfer GmbH).

#### 4.2. RESULTS OF CATALYTIC OXIDATION OF VOCs

Gas chromatographic analysis of VOCs emitted in motor exhaust made it possible to determine the following major air pollutants divided into three groups:

- aromatic hydrocarbons (benzene, toluene, xylene, ethylbenzene);
- alkanes (pentane, hexane, heptane);
- oxy-derivatives (acetaldehyde, butyr aldehyde, acrolein, acetone).

Table 3 presents typical concentration of detected VOCs, depending on the engine load.

Table 3

Typical concentrations of detected VOCs  
at idle run, 30 and 60% engine loads

Compound	Concentration, mg/m <sup>3</sup>		
	Idle run	30%	60%
Benzene	52.7	46.1	20.7
Toluene	33.8	68.0	49.5
Xylene	30.3	30.0	23.1
Ethylbenzene	12.4	2.3	9.7
Pentane	36.3	20.2	41.1
Hexane	40.7	18.7	36.7
Heptane	24.8	12.5	21.9
Acetaldehyde	33.1	20.8	53.0
Butyr aldehyde	3.2	6.7	7.0
Acrolein	2.0	2.4	0.2
Acetone	1.3	1.2	4.5

Of these, aromatic hydrocarbons were found at the highest concentration, their maximum total concentration reached 130 mg/m<sup>3</sup> at idle run. The mass fraction of aromatics at different engine load varied from 50 to 83%. The mass fraction of alkanes ranged between 14 and 46%. Oxy-derivatives were detected at lower concentration than hydrocarbons. Generally, the concentration of VOCs decreased with increasing engine load. The increase of temperature of engine after 75 minutes of its

work resulted in a slight decrease of the concentration of aromatic hydrocarbons and an increase of the concentration of the other two groups of organic compounds.

The results of conversion efficiency of VOCs grouped in three classes – aromatics (AH), alkanes (A) and oxy-derivatives (OD) – for selected engine load, in the presencen of both catalysts under investigation are shown in figure 4.

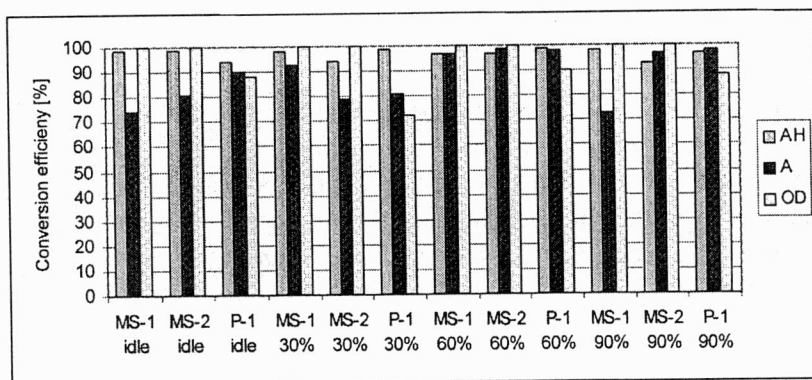


Fig. 4. Conversion efficiency of aromatic hydrocarbons (AH), alkanes (A) and oxy-derivatives (OD) over MS-1, MS-2 and P-1 catalysts, depending on the engine load

The activities of all catalysts investigated were similar and relatively high, the total conversion efficiency of VOCs varied from 70 to c.a. 100%. The most catalytically reactive pollutants were aromatic hydrocarbons, their conversion efficiency varied from 93 to 100%, independently of the engine load. Over both catalysts MS-1 and MS-2 on metallic monolithic support the oxy-derivatives were oxidized almost completely. Only in the presence of P-1 (on cordierite support), the conversion efficiency of oxy-derivatives was lower, i.e. it reached 90%, and decreased to 73% at the engine load of 30%. Alkanes were most resistant to oxidation, their conversion efficiency for both catalysts ranged between 72 to 99%.

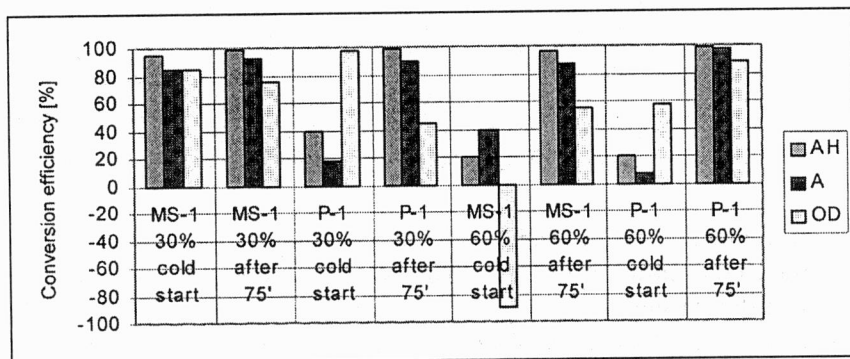


Fig. 5. Conversion efficiency of aromatic hydrocarbons (AH), alkanes (A) and oxy-derivatives (OD) over MS-1 and P-1 measured for "cold start" and after 75 minutes of engine work



The catalyst activity versus the engine temperature ("cold start" and after 75 minutes of engine work) is presented in figure 5. Generally, catalyst activity was much lower for the cold engine, which resulted from low temperature of exhaust gases (~250 °C), too low for the catalyst effective work. In these conditions, aromatics were oxidized with 20–40% efficiency only, while after 75 minutes of the engine work this efficiency reached 98–99%. Over MS-1, for "cold start" and the engine load of 60%, the concentration of oxy-derivatives in flue gas after the catalyst was even higher than that before the converter. Probably, some of hydrocarbons were oxidized only partially – to aldehydes, typical products of incomplete oxidation.

#### 4.3. CATALYTIC CONVERSION OF PAHs

The concentration of PAHs detected in exhaust gases was very low (table 4), 2–3-fold lower than that of VOCs. Only when the engine worked at a deficit of oxygen ( $\lambda < 1$ ) the concentration of naphthalene was distinctly higher than for regular engine work at  $\lambda \sim 1$ .

Table 4

Concentration of PAHs in exhaust gases  
at 30 and 60% engine loads

Compound	Concentration, $\mu\text{g}/\text{m}^3$	
	30%, $\lambda \sim 1$	60%, $\lambda < 1$
Naphthalene	2.86	206.97
Acenaphthylene	23.9	10.77
Acenaphthene	4.86	n.d.
Fluorene	0.32	n.d.
Anthracene	0.9	n.d.
Fluoranthene	0.9	1.7
Pyrene	0.85	3.2

n.d. – not detected.

PAHs conversion efficiency was investigated only over MS-1. The results are presented in figure 6.

At 30% engine load, almost all PAHs in the exhaust gas were completely oxidized. Only traces of acenaphthene were detected in the flue gas – its conversion efficiency reached 84%. For the series with the fuel combustion with a deficit of oxygen ( $\lambda < 1$ ), the potential condition for soot generation, which can partially block the active sites of the catalyst, the catalyst activity decreased and the efficiency of PAHs oxidation was evidently lower. Similar catalyst activities in the process of PAHs oxidation were

reported in our earlier papers [9]. When the engine was adjusted to the correct condition ( $\lambda \sim 1$ ), the catalyst regained its initial activity.

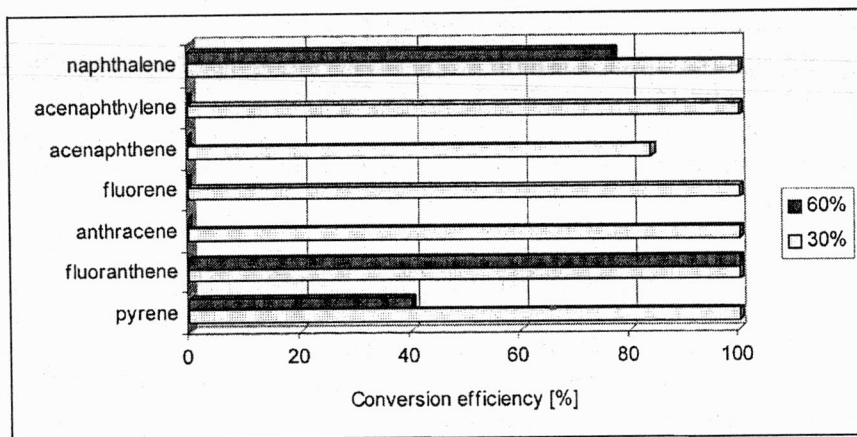


Fig. 6. Conversion efficiency of the PAHs detected over MS-1 for 30 and 60% engine loads

## 5. CONCLUSIONS

All manufactured noble metal catalysts on metallic support were very active in the test reaction of toluene oxidation. Over all catalysts under investigation, at 240 °C toluene was oxidized with 90% efficiency. The catalyst activity in heptane and selected oxy-derivatives oxidation was slightly poorer. The process of some oxy-derivatives oxidation – ethanol and ethyl acetate – ran via acetaldehyde, typical product of incomplete oxidation detected in reaction gas. Perovskite catalyst showed very high activity in the oxidation of hydrocarbons and oxy-derivatives, comparable with the activity of platinum catalyst.

Chlorinated hydrocarbons were more resistant to catalytic oxidation. Their catalytic reactivities decreased with an increasing number of chlorine atoms in the molecule, irrespective of the catalyst used. Hydrochloric acid was found to be the main chlorine-containing reaction product. Only over platinum catalyst, at the reaction temperature higher than 400 °C, chlorine was detected in the flue gas, but at much lower concentration than hydrochloric acid. The test of toluene oxidation carried out after 100–150 hours of M-3 and M-4 catalyst exposure to chlorinated compounds showed that the activities of both catalysts were similar to those of fresh contacts. After tests with chlorine compounds, no physical changes of the catalyst surface (attrition or crushing of the active phase or the washcoat) were observed.

All catalysts under investigation showed very high activities in the oxidation of organic compounds emitted in motor exhaust gases. For a regular engine work under lean-burn conditions, the conversion efficiency of aromatic hydrocarbons was higher than 90%. Alkanes and oxy-derivatives were oxidized with 70–100% efficiency, de-

pending on the engine load and duration of motor work. PAHs were oxidized with higher efficiency than VOCs, and during regular engine work were oxidized almost completely.

The results of the investigations presented showed that the manufactured noble metal catalysts on metallic or cordierite monolithic support were active in the oxidation of organic compounds, differing their chemical structures. It is necessary to point out that catalyst activity depends not only on the active ingredient, but also on the support preparation and the washcoat composition. These modern catalysts could be effectively used in the process of organic compound oxidation both from industrial and motor exhaust gases.

#### REFERENCES

- [1] MENDYKA B., MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Effect of chlorine compounds on the deactivation of platinum catalysts*, Catal. Today, 1992, Vol. 11, 597–610.
- [2] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Catalytic oxidation of trichloroethylene in two-component mixtures*, Environ. Prot. Eng., 1998, Vol. 24, 113–122.
- [3] TAYLOR K.C., *Automotive catalytic converters*, Catal. Automobile Poll. Control, Elsevier Sci. Publ., 1987, 97–116.
- [4] WINDAWI H., WYATT M., *Catalytic destruction of halogenated volatile organic compounds*, Platinum Metal Rev., 1993, Vol. 37, 186–194.
- [5] NOORDALLY E., RICHMOND J.R., TAHIR S.F., *Destruction of volatile organic compounds by catalytic oxidation*, Catal. Today, 1993, Vol. 17, 359–366.
- [6] GONZALEZ-VALESCO J.R., ENTRENA J., *Preparation, activity and durability of promoted platinum catalysts for automobile exhaust control*, Appl. Catal. B, Environ., 1994, Vol.3, 191–204.
- [7] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Combustion of volatile organic compounds in component mixtures over monolithic perovskite catalysts*, Catal. Today, 2000, Vol. 59, 269–278.
- [8] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., *Volatile organic compounds oxidation over metal oxide catalysts*, Environ. Prot. Eng., 1999, Vol. 25, 105–114.
- [9] MUSIALIK-PIOTROWSKA A., SYCZEWSKA K., MENDYKA B., *Catalytic oxidation of organic compounds including PAHs from motor exhaust gases*, Environ. Prot. Eng., 1998, Vol. 24, 123–132.

#### KATALITYCZNE UTLENIANIE ORGANICZNYCH ZANIECZYSZCZEŃ POWIETRZA EMITOWANYCH W PRZEMYSŁOWYCH GAZACH ODLOTOWYCH I SPALINACH SILNIKOWYCH

Przedstawiono najnowsze osiągnięcia Zespołu Katalizy Ekologicznej w preparatyce monolitycznych katalizatorów na bazie metali szlachetnych na nośniku metalicznym i kordierytowym. Ich aktywność testowano w reakcji utleniania typowych par rozpuszczalników emitowanych z zakładów przemysłowych oraz lotnych związków organicznych i wielopierścieniowych węglowodorów aromatycznych (WWA) ze spalin silnikowych. Katalizatory wytworzone na bazie Pt, Pd, Rh oraz jeden perowskitowy wykazały wysoką aktywność w utlenianiu węglowodorów, połączeń tlenowych oraz WWA, niższą natomiast w utlenianiu połączeń chloroorganicznych. Nie stwierdzono dezaktywacji katalizatorów w obecności związków chloru.

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