

ANNA MUSIALIK-PIOTROWSKA\*, BARBARA KUCHARCZYK\*\*

## METHANE COMBUSTION AND OXIDATION OF SELECTED VOLATILE ORGANIC COMPOUNDS OVER PEROVSKITE CATALYSTS

Methane combustion and oxidation of selected volatile organic compounds (*n*-hexane, toluene and acetone) over perovskite monolithic catalysts on metallic supports were tested. Catalysts varied in the active phase composition ( $\text{LaMnO}_3$  alone or with addition of silver and  $\text{LaCoO}_3$ ) and its content in the catalyst. Results of XRD and scanning microscopy analyses of manufactured catalysts are presented. They showed very uniform distribution of perovskite crystals, as well as La, Mn and Ag elements on the surfaces of catalysts.  $\text{LaCoO}_3$  catalyst showed the highest efficiency in process of methane combustion. The most active catalyst in the oxidation of volatile organic compounds (VOCs) was  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$  with the highest silver content (25 atom.%) and with the highest content of active ingredient (27 wt.%).

### 1. INTRODUCTION

Catalytic oxidation seems to be an attractive method of controlling organic air pollutants emitted with industrial waste gases. On the other hand, catalytic combustion can be a promising way to produce environmentally clean energy which allows us to burn gaseous fuels, e.g. methane, at a temperature ranging from 550 to 800 °C, evidently lower than that of flame combustion (> 1000 °C), without production of secondary air pollutants or undesired by-products such as  $\text{NO}_x$  or CO.

Catalysts applied in such processes are traditionally based on platinum group metals. The search for much cheaper substitutes of noble metal catalysts had led to the study of various mixed metal oxides like perovskites of overall structure  $\text{ABO}_3$ , where A is a rare earth or alkali earth ion and B is a transition metal ion. It has been found that  $\text{LaMO}_3$  structures, where M = Mn, Co or Ni, are particularly efficient in total oxidation of volatile organic compounds (VOCs) in air [1]–[3]. Both cations can be

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\* Wrocław University of Technology, Institute of Environment Protection Engineering.

\*\* Wrocław University of Technology, Institute of Inorganic Chemistry and Mineral Fertilizers, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

partially substituted for the others to form a structure like  $A_{1-x}A'_xB_{1-y}B'_yO_{3 \pm \delta}$ . This results in the change of composition and symmetry of perovskite and can affect its catalytic properties as well as chemical and thermal stability. Overstoichiometric content of ions in the position B and oxygen contents  $O_{3 \pm \delta}$  in perovskite structure enhanced an overall catalyst activity [4], [5]. In methane combustion, the reactivity of some catalysts tested decreased in the following order [4]:



The manufacture of bulk or supported metal oxide catalysts in granular form is a well-known process. Noticeable advantages of monolithic form of the catalyst – low pressure drop, uniform flow distribution of reagents within the honeycomb matrix, easier accessibility of catalyst active centers to the reaction gas – make this form interesting also in the case of industrial waste gas control. Very few studies have been focused on the preparation of perovskite-based monolithic catalysts manufactured by washcoating ceramic monolithic support or by directly extruding active honeycomb-type perovskite phase. Mechanical strength of directly extruded catalytic monolith is usually too low, and addition of any inert binder results in the decrease of catalyst activity. The impregnation of monolithic support with the slurry of perovskite precursor seems to be more efficient way in the catalyst preparation. Some catalysts, basing on  $\text{LaMnO}_3$  perovskite on cordierite monolithic support, prepared in collaboration with the University of Applied Technology in Dresden, Germany, showed very high activity in the oxidation of selected VOCs in air, while in oxidizing oxy-derivatives their activity was even higher than that of platinum catalysts [6], [7].

The monolithic cordierite thin-wall supports are not produced in Poland, hence it was interesting to manufacture perovskite-type catalysts, differing in chemical composition of active phase, on metallic monoliths of heat-resisting steel, with  $\gamma$ -alumina washcoat. The activity of such catalysts was investigated in the combustion of selected hydrocarbons – methane, *n*-hexane and toluene. Thermal stability and durability of the catalysts were also tested by “thermal shocks” aging cycles.

## 2. CATALYSTS

Five catalysts were manufactured for the purpose of the study: two of them basing on  $\text{LaMnO}_3$ , differing in the active phase contents, next two – on the same  $\text{LaMnO}_3$  bases, but with  $\text{La}^+$  ions partially substituted for  $\text{Ag}^+$  ions, and one – basing on  $\text{LaCoO}_3$ .  $\text{LaMnO}_3$  perovskite precursor was prepared by co-precipitation of hydroxide deposit of adequate metal from water solution of their nitrates with polyvinyl alcohol and  $\text{NaOH}$ . In order to obtain adequate perovskite, the precipitate was dried and calcinated at 600–750 °C. The specific surface area of perovskite powder prepared in such a way reached 26 m<sup>2</sup>/g.  $\text{LaCoO}_3$  perovskite was co-precipitated with  $\text{NaOH}$ ,

without alcohol, and calcinated at 1200 °C. At so high temperature only perovskite form was obtained, but the specific surface area of such catalyst did not exceed 2 m<sup>2</sup>/g. At lower calcination temperature, beside perovskite structure also the other metal oxides were detected. Metallic monolithic supports from heat-resisting steel, chemically pretreated by etching in acids, were coated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the addition of rare earth elements. The contents of the washcoat reached 2.5 wt.%. In the case of LaMnO<sub>3</sub> perovskite, the supports prepared in such a way were impregnated with the slurry of perovskite precursor and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, in mass proportion of 4 : 1, dried and calcinated. LaCoO<sub>3</sub>-based catalyst was impregnated by immersion in the slurry of perovskite precursor only, without Al<sub>2</sub>O<sub>3</sub>, with addition of citric acid, dried and calcinated at 500 °C. For both active phases, the procedure of support immersion in the perovskite slurry and drying was repeated several times.

The activity of manufactured catalyst on metallic monolithic support in the process of VOCs oxidation was compared with the activity of La<sub>0.5</sub>Ag<sub>0.5</sub>MnO<sub>3</sub>-type catalyst on cordierite monolithic support with active phase contents of 12 wt.%. Description of cordierite and metallic supports is presented in table 1.

Table 1

Description of the monolithic supports applied

| Parameter                        | Cordierite             | Metallic support       |
|----------------------------------|------------------------|------------------------|
| Shape of cell                    | square                 | triangle               |
| Density of cells/cm <sup>2</sup> | 32                     | 112                    |
| Length of cell side, mm          | 1.45                   | 1.37                   |
| Wall thickness, mm               | 0.3                    | 0.05                   |
| Open area, %                     | 67                     | 84                     |
| Dimension of catalyst block, mm  | $h = 73, \varphi = 21$ | $h = 70, \varphi = 24$ |

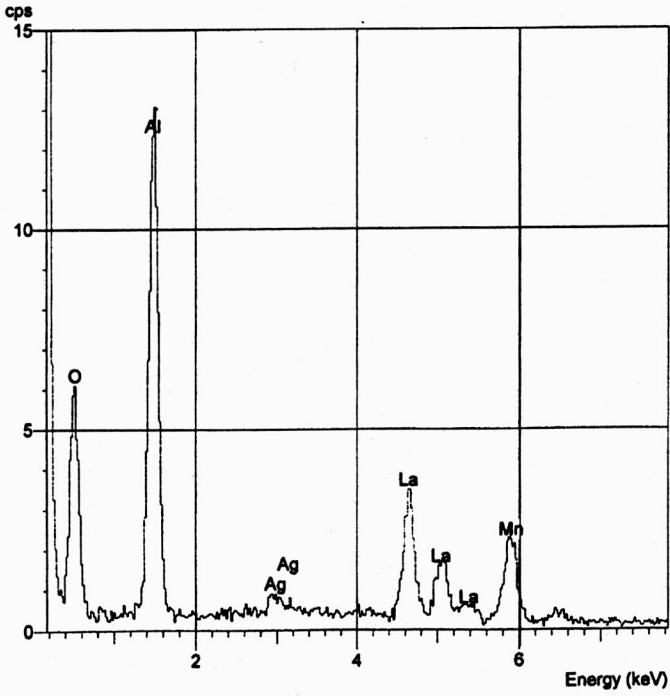
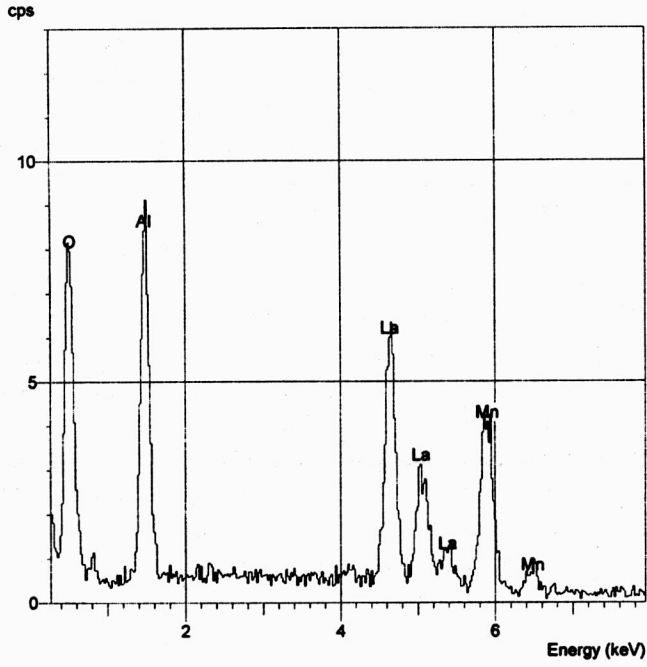
Table 2

Description of the catalysts manufactured

| Catalyst | Active phase   | Contents of active phase (wt.%) |
|----------|--|---------------------------------|
| PEM-1    | LaMnO <sub>3</sub>                                     | 13.6                            |
| PEM-2    | LaMnO <sub>3</sub>                                     | 19                              |
| PEM-3    | La <sub>0.9</sub> Ag <sub>0.1</sub> MnO <sub>3</sub>   | 14                              |
| PEM-4    | La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub> | 27                              |
| PEC-1    | LaCoO <sub>3</sub>                                     | 19                              |

Description of manufactured catalysts on metallic supports is presented in table 2.

XRD analysis of the surface of selected catalysts, i.e. PEM-2, PEM-3 and PEC-1, was carried out, and the results are presented in figure 1. The contents (in % atom.) of particular elements on the catalyst surfaces are shown in table 3.



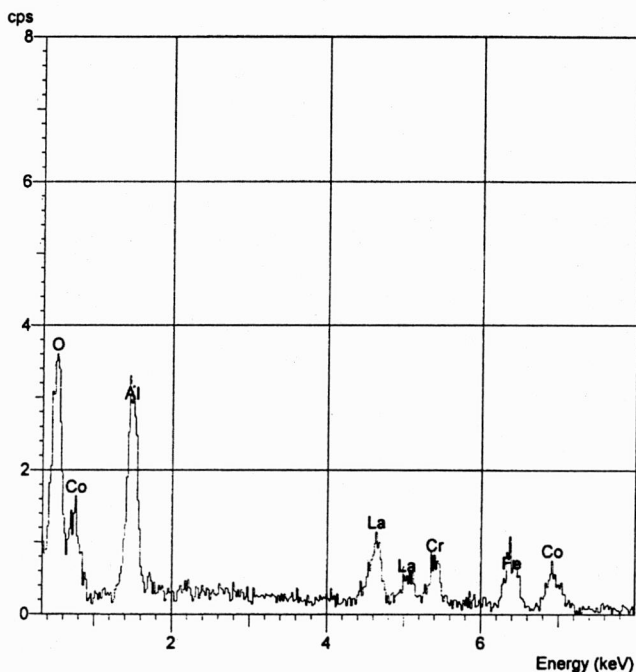


Fig. 1. Results of XRD analysis: a – PEM-2, b – PEM-3, c – PEC-1

Table 3

Contents of the elements of catalyst active phases

| Catalyst | Element contents (% atom.) |       |      |     |      |      |
|----------|----------------------------|-------|------|-----|------|------|
|          | O                          | Al    | Mn   | Co  | La   | Ag   |
| PEM-2    | 63.38                      | 17.77 | 9.45 | –   | 9.10 | –    |
| PEM-3    | 62.58                      | 26.06 | 5.27 | –   | 5.4  | 0.69 |
| PEC-1    | 79.25                      | 11.46 | –    | 5.0 | 4.29 | –    |

Spectrum (figure 1) showed the presence of perovskite elements (La, Mn in PEM-2 and La, Mn and Ag in PEM-3) as well as oxygen and aluminum. High content of aluminum – 17.77% and 26.06% for PEM-2 and PEM-3, respectively – results from the method of catalysts preparation – by impregnation with the slurry containing both perovskite precursor and  $\gamma$ - $\text{Al}_2\text{O}_3$  as binder. According to the overall contents of the active phase in catalysts PEM-2 and PEM-3, lanthanum and manganese contents on PEM-2 surface were nearly two times higher than those on PEM-3 surface, with simultaneously lower aluminum contents. Aluminum was found on the catalyst surface, because it was present in the slurry as a binder incorporated into perovskite active phase and as the wash-coat material. The map of the analyzed surface of PEM-3 (figure 2)

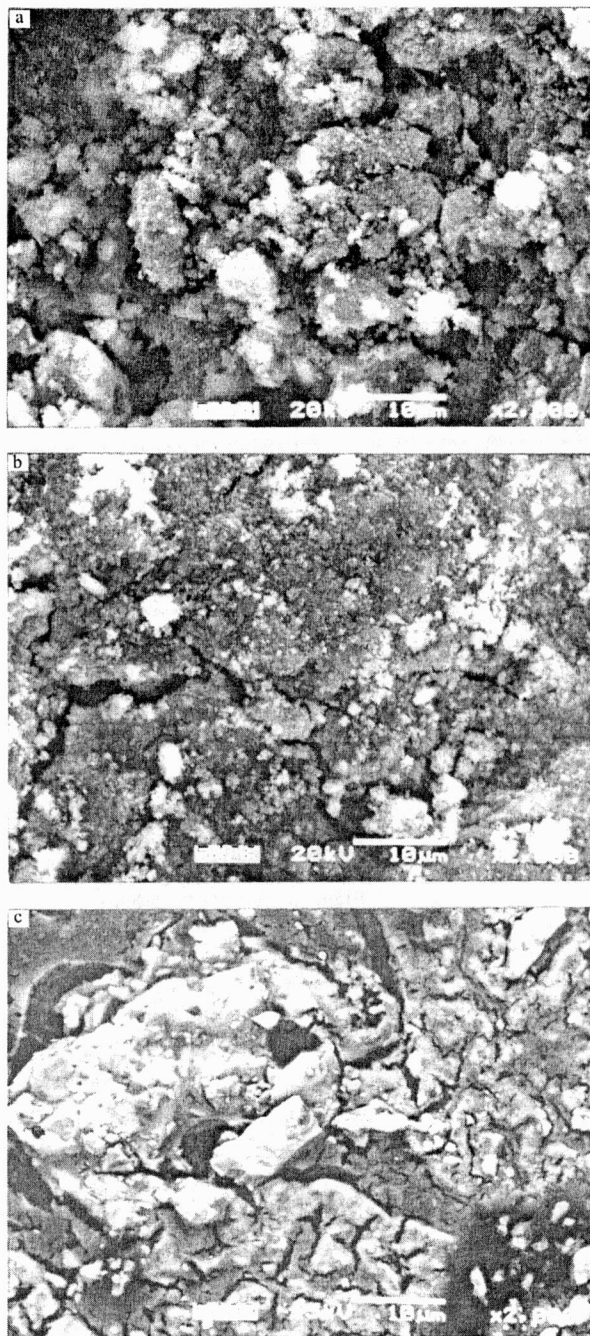


Fig. 2. Micrographs of selected catalyst surfaces:  
a – PEM-2, b – PEM-3, c – PEC-1

showed very uniform distribution of all elements of the active phase – lanthanum, manganese and silver. On PEC-1 surface, PEC-1 catalyst was prepared by impregnation with perovskite precursor slurry only, without aluminium as binder. On the surface of this catalyst, beside lanthanum, cobalt and oxygen from the active phase, also aluminum from the wash-coat, as well as iron and chromium from the metallic support were found in the spectrum. This finding can be attributed to too thin layer of the active phase and its non-uniform deposition on the wash-coat surface.

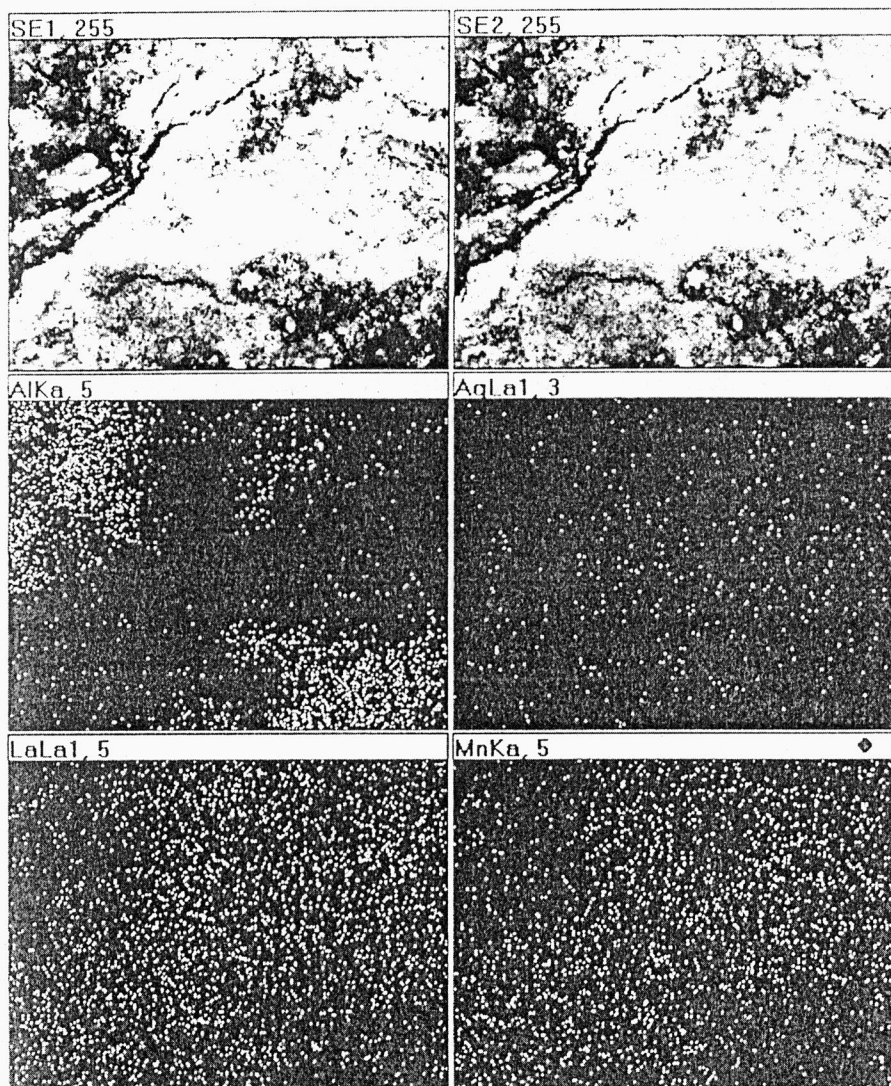


Fig. 3. Map of the distribution of active elements on the surface of the catalysts PEM-3

The surfaces of selected catalyst samples were observed with scanning microscope. The micrographs are shown in figure 3. Microanalysis of PEM-2 and PEM-3 surfaces showed good covering of wash-coat surface with the active ingredient. The surface of PEM-2 is uniformly covered with crystals of 10–15  $\mu\text{m}$ . On PEM-3 surface, the crystals are smaller and their number is lower. Silver can also be observed in the form of very small crystals. On the surfaces of both catalysts the crystals have highly developed surfaces. The surface of PEC-1 sample is quite different. On this surface there occur crushed crystals with smooth surfaces, generally bigger compared to the crystals on the LaMn-type catalyst. Such view can be attributed to lower specific surface area of  $\text{LaCoO}_3$ , which resulted in lower catalyst activity in the processes of volatile organic compounds oxidation compared to La-Mn-based catalysts.

The thermal resistance of a wash-coat and active phase of manufactured catalysts to thermal shocks was investigated [8]. Tests of "thermal shocks" were performed in a specially constructed oven, which enables quick heating of the tested sample of catalyst to a temperature of 1000  $^{\circ}\text{C}$ , and cooling it down to a room temperature. One cycle of the "thermal shock" lasted 30 s, and each catalyst passed through nearly 4000 cycles. The results of investigation measured in term of a relative decrease of catalyst weight during aging tests showed very high resistance of manufactured catalysts to thermal shocks. The smallest relative loss of catalyst weight was observed for  $\text{LaCoO}_3$  and after 4000 cycles it reached 1.3% only, hence this catalyst seems to be particularly suitable for methane combustion.

### 3. METHODS OF CATALYST ACTIVITY INVESTIGATION

Tests of catalyst activity were carried out for the combustion of:

- methane,
- *n*-hexane – aliphatic hydrocarbon,
- toluene – aromatic hydrocarbon,
- acetone – oxy-derivative compound.

Tests were performed in electrically heated quartz reactors. The reaction temperature measured inside the catalyst block ranged from 250 to 500  $^{\circ}\text{C}$  when VOCs were oxidized, and from 300 to 750  $^{\circ}\text{C}$  – for methane combustion. The reaction mixture of each of VOCs in air was prepared by mixing the vapours of the compound tested with air to obtain its desired concentration of 1  $\text{g}/\text{m}^3$ . The concentration of methane in air reached 1% vol. The tests were conducted at gas space velocities of 5800 and 8000  $\text{h}^{-1}$  for methane and VOCs, respectively. Catalyst activity was estimated as conversion efficiency and measured from the inlet and outlet concentrations of oxidized compound. The concentration of methane was measured with SNIFFER (Bacharach) gas analyzer. Quantitative analysis of selected VOCs was carried out by gas-chromatography, with Perkin-Elmer GC (FID, 1.8 m column packed with 10% PEG on Chromosorb W). The temperature of column amounted 73  $^{\circ}\text{C}$ , while that of injector and detector – 150  $^{\circ}\text{C}$ .



## 4. RESULTS OF CATALYSTS ACTIVITY INVESTIGATIONS

The temperatures of 50 and 90% conversion of toluene, *n*-hexane and acetone as well as 50 and 70% of methane combustion are presented in table 4. The results of methane conversion are plotted in figure 4.

Table 4

| Catalyst | Temperatures [°C] of adequate combustion efficiency |     |                  |       |         |     |         |     |
|----------|---|-----|------------------|-------|---------|-----|---------|-----|
|          | Methane   |     | <i>n</i> -hexane |       | Toluene |     | Acetone |     |
|          | 50%   | 70% | 50%              | 90%   | 50%     | 90% | 50%     | 90% |
| PEM-1    | 630   | 780 | 375              | > 500 | 360     | 405 | 280     | 330 |
| PEM-2    | 620   | 750 | 370              | 440   | 325     | 400 | 260     | 300 |
| PEM-3    | 600   | 770 | 370              | 440   | 360     | 425 | 275     | 310 |
| PEM-4    | 600   | 770 | 310              | 405   | 300     | 360 | 235     | 260 |
| PEC-1    | 630   | 695 | 390              | >>470 | 345     | 400 | 300     | 360 |
| PER-Ag   | -   | -   | 325              | 370   | 300     | 370 | 240     | 260 |

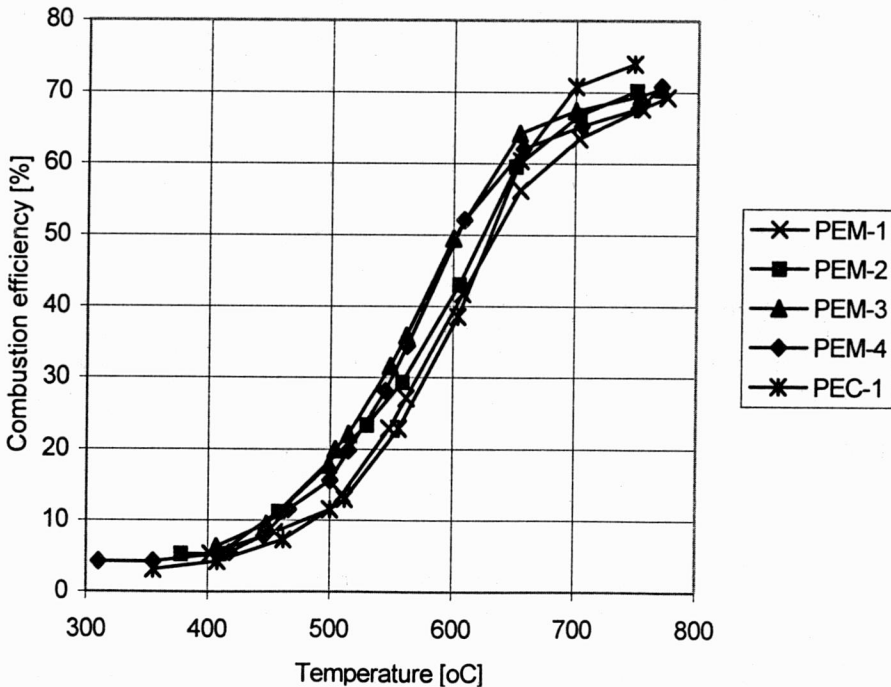


Fig. 4. Methane combustion over catalysts

50% combustion of methane was observed at temperature ranging from 600 °C (PEM-3, PEM-4) to 630 °C (PEM-1, PEC-1). 70% combustion of methane, only over

LaCoO<sub>3</sub>, was achieved at 695 °C; for the other catalysts this temperature exceeded 700 °C. Even at the highest reaction temperatures of 780 °C, the maximum combustion efficiency reached 75% for LaCoO<sub>3</sub>, and 70% only for catalysts basing on LaMn-type perovskites. Generally, higher efficiency of methane combustion was observed for the catalysts with increased active phase contents (e.g. catalyst PEM-1 and PEM-2 containing 13.6 wt.% and 19 wt.% of active phase, respectively) or over the catalyst with La<sup>+</sup> ions partially substituted for silver ions, even in 10 atom.% only. The increase of silver content to 25 atom.% did not affect the catalyst activity in methane combustion.

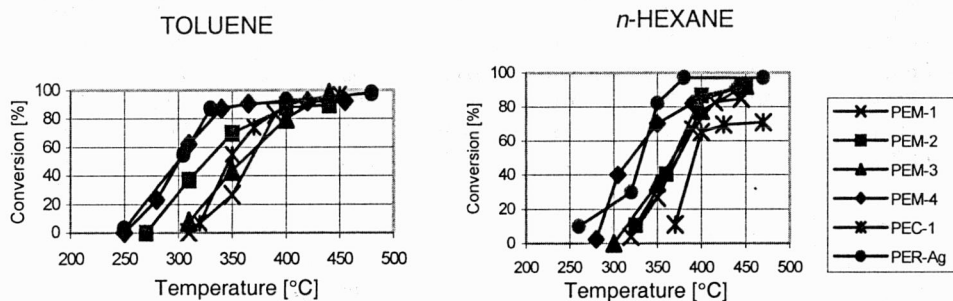


Fig. 5. Conversion of toluene and *n*-hexane over catalysts

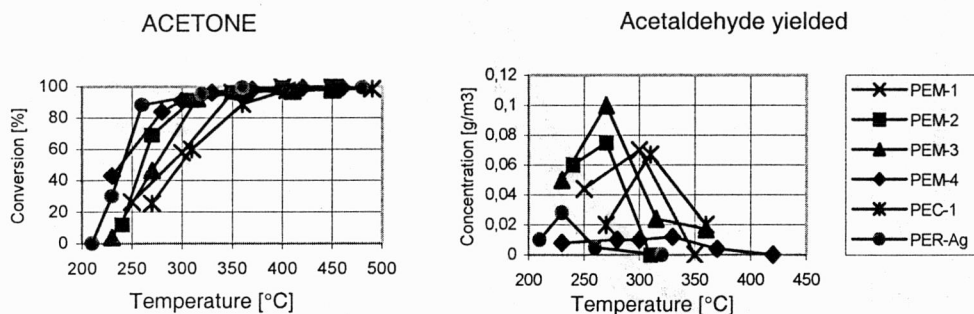


Fig. 6. Conversion of acetone over catalysts with the concentration of acetaldehyde yielded

Typical oxidation of solvent vapours proceeded at much lower temperature than that necessary for methane combustion (figures 5 and 6). Selected hydrocarbons were oxidized to CO<sub>2</sub> and water, no other organic compounds were detected in the flue gas. In the course of acetone oxidation, acetaldehyde – typical product of incomplete oxidation – was detected in a gas stream after each catalyst under investigation. The catalyst PEM-4 with the highest active phase content (27 wt.%) and the greatest ad-

mixture of silver (25 atom.%) was the most active in the oxidation of each of VOCs. 50% conversion of *n*-hexane and toluene was observed at 310 °C and 300 °C, respectively. For their conversion with 90% efficiency, the respective temperatures of 405 °C and 360 °C were necessary. PEM-4 was the most active in acetone oxidation as well, and for its 50% and 90% conversion, the temperatures of 235 °C and 260 °C were needed. Simultaneously, in the course of acetone oxidation, the concentration of acetaldehyde yielded was very low, and its maximum concentration (at 240 °C) did not exceed 0.017 g/m<sup>3</sup>.

Among the other catalysts on metallic monolithic support, the most active in toluene oxidation was PEM-2 (LaMnO<sub>3</sub>) with relatively high perovskite contents (19 wt.%). 50% and 90% conversion of toluene was observed at 325 °C and 400 °C, respectively. Addition of silver (10 atom.%) simultaneously with the decrease of the active phase content to 14 wt.% did not enhance the catalyst activity, and over PEM-3 the temperature at which 50% and 90% conversion of toluene took place rose up to 360 °C and 425 °C, respectively. The activity of LaCoO<sub>3</sub> catalyst in toluene oxidation did not differ from that of LaMnO<sub>3</sub> catalysts, and was similar to the activity of PEM-2 and PEM-3.

In the reaction of *n*-hexane oxidation, catalysts PEM-2 and PEM-3 showed similar activity, 50% and 90% conversion was achieved at 370 °C and 440 °C. These two catalysts differed both in active phase content and its chemical composition. It can be concluded that similar activity in *n*-hexane oxidation showed catalyst with higher perovskite content (19 wt.%) and the catalyst with reduced up to 14 wt.% perovskite content but with 10 atom.% addition of silver (La<sub>0.9</sub>Ag<sub>0.1</sub>MnO<sub>3</sub>). The catalyst basing on LaCoO<sub>3</sub> exhibited very low activity in *n*-hexane oxidation; even at 475 °C its conversion did not exceed 70%.

Acetone was found to be the most reactive among the compounds being oxidized, and with 90% efficiency was oxidized at 300–320 °C over nearly all catalysts (except PEM-1 and PEC-1). On the other hand, the concentration of acetaldehyde – the product of incomplete oxidation of ketone – varied from one catalyst to another. The highest concentrations of aldehyde produced in the presence of PEM-3 and PEM-2 were found at 270 °C, and reached 0.1 and 0.078 g/m<sup>3</sup>, respectively. Aldehyde concentration in flue gas produced over PEM-1 and PEC-1 amounted to 0.07 g/m<sup>3</sup> at 300–310 °C.

The results of VOCs oxidation showed without doubt that the activity of perovskite La<sub>0.5</sub>Ag<sub>0.5</sub>MnO<sub>3</sub>-type catalyst on cordierite monolithic support was higher than that of similar catalyst, but on the metallic monolithic support. 90% efficiency of toluene and *n*-hexane oxidation was found at 370 °C, and acetone – at a temperature even by 110 deg lower. The concentration of acetaldehyde in the flue gas was very low, and reached 0.03 g/m<sup>3</sup> at 230 °C. It is very difficult to compare the activity of all these catalysts. They differed both in silver and in the active phase contents. In PER-Ag on the cordierite support, silver content reached even 50 atom.%, and despite a slightly lower active phase content in this catalyst, such a high activity probably should be attributed to a high silver content. It is known that the addition of silver enhanced the activity of Mn-

basing catalysts. WATANABE et al. [9] had found that the amount of oxygen adsorbed on and desorbed from Ag-Mn catalyst was 2.9 times higher compared to  $Mn_2O_3$ . It was suggested that manganese oxide supplied oxygen to silver, maintaining its high oxidative state, which resulted in an efficient donation of oxygen over the whole catalyst [9].

## 5. CONCLUSIONS

The aim of the study was to find out the possibility of preparing perovskite-type active catalyst on metallic monolithic support. It is much more difficult to prepare metal-oxide catalysts on such a support than on cordierite support. Metallic support needed earlier pretreatment, i.e. etching in acids, washing and drying. Next a  $\gamma-Al_2O_3$  wash-coat was deposited. The procedure of immersion in the perovskite slurry and drying the support thus prepared was repeated several times. An active catalyst on cordierite support did not need earlier wash-coat deposition and usually was impregnated with the perovskite slurry two times only.

The activity of manufactured catalysts, varying in the chemical composition of active phase, was high enough and depended on the oxidized compound. The catalyst based on  $LaCoO_3$  at a temperature above  $650^\circ C$  showed higher activity in methane combustion than  $LaMnO_3$ -type catalysts. Simultaneously, its activity in VOCs oxidation was distinctly lower. On the other hand, this catalyst showed very high thermal stability and resistance to "thermal shocks".

The catalyst PEM-4 of the highest active phase content (27 wt.%) and silver content (25 atom.%) was the most active in the oxidation of selected hydrocarbons and acetone. The catalyst PER-Ag on the monolithic cordierite support based on  $La_{0.5}Ag_{0.5}MnO_3$ , with an active ingredient content of 12 wt.% only showed similar or even higher activity compared to PEM-4 in selected VOCs oxidation.

Further investigations will be concentrated both on a development of the highly active phase composition and a simplification of the catalyst preparation procedure.

## ACKNOWLEDGEMENT

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#### SPALANIE METANU

#### I UTLENIANIE WYBRANYCH LOTNYCH ZWIĄZKÓW ORGANICZNYCH NA KATALIZATORACH PEROWSKITOWYCH

Przedstawiono wyniki badań nad skutecznością spalania metanu, *n*-heksanu i toluenu na katalizatorach perowskitowych na monolitycznych nośnikach metalicznych. Katalizatory różniły się składem czynnika aktywnego (LaMnO<sub>3</sub>, sam i z dodatkiem srebra, oraz LaCoO<sub>3</sub>) oraz jego zawartością. Przedstawiono wyniki analizy rentgenograficznej i mikroskopowej wybranych kontaktów. Wykazały one równomierny rozkład La, Mn i Ag na powierzchni. Katalizator na bazie LaCoO<sub>3</sub> wykazał najwyższą aktywność w spalaniu metanu. W utlenianiu *n*-heksanu i toluenu najaktywniejszy był kontakt La<sub>0.75</sub>Ag<sub>0.25</sub>MnO<sub>3</sub> z największym dodatkiem srebra (25% mas.) i najwyższą zawartością czynnika aktywnego.

