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OXIDATION OF ORGANIC AIR POLLUTANTS OVER NOBLE METAL-MODIFIED PEROVSKITE-BASED MONOLITHIC CATALYSTS

Five catalysts on monolithic metallic support, based on $LaMnO_3$ perovskite alone or with lanthanum partially substituted for silver ($La_{0.95}Ag_{0.05}MnO_3$) or platinum ($La_{0.9}Pt_{0.1}MnO_3$, $La_{0.8}Pt_{0.2}MnO_3$), were prepared and tested in the oxidation of methane, toluene, n-hexane and ethanol. Of the catalysts manufactured, the catalyst with lower platinum content ($La_{0.9}Pt_{0.1}MnO_3$) showed the highest activity in the oxidation of each compound tested, despite a relatively low specific surface area (3.39 m^2/g). As for the $La_{0.9}Pt_{0.1}MnO_3$ catalyst, the analysis of pore distribution showed a high proportion of the pores both 15 and 60 nm in diameter; as for the other catalysts, the pores of 30–35 nm diameters prevailed. All noble metal-doped catalysts were slightly less resistant to thermal shocks than the $LaMnO_3$-based catalysts.

1. INTRODUCTION

Anthropogenic emission of volatile organic compounds (VOCs) is a serious problem in environmental engineering. VOCs emitted into the atmosphere are formed in enameling and varnishing processes, during production and manufacturing of plastics, pharmaceuticals, foods as well as in different process of chemical industry. A great deal of antropogenic methane emission is due to lean-burn natural gas fuelled vehicles, animal farms, biological processes used for solid wastes and wastewater treatment, coke and biomass combustion, etc. Methane, being the simplest saturated alkane, is the most difficult hydrocarbon to oxidize catalytically and requires much higher-reaction temperature than other organic compounds.

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Catalytic oxidation seems to be the most interesting method of organic emission control. A high price of noble metals (Pt and Pd) has spurred the search for new catalytic systems based on cheaper metal oxides. Of these, perovskites of the general formula ABO_3 (where A is a lanthanide or the ion of alkaline earth metals and B a transition metal ion) were found to be most active and most heat resistant, and thus suitable for the oxidation of organic air pollutants and carbon monoxide [1]–[3]. It has been reported that $LaMO_3$ perovskites with M = Mn, Co or Ni are particularly suited for total VOCs oxidation [4]–[6]. A partial substitution of ions in A and/or B position for A′ and B′ ions produces crystal lattice defects, thus upgrading their catalytic properties [7]–[9].

Sparce information can be found in the literature on the modification of perovskites by addition of noble metals. Addition of silver, particularly to a Mn-containing active phase, improves catalyst activity by a three-fold increase in oxygen storage [10], [11]. The incorporation of noble metals into a perovskite structure protects metals against sintering, agglomerating or reaction with the support material. Moreover, it has been reported that Pt, Rh or Pd partially incorporated in B position migrate between the bulk structure and the surface, depending on the oxygen concentration in the exhaust gases [12], [13]. Our previous study has shown that a Pt-doped $LaMnO_3$ catalyst on monolithic metallic support, prepared in collaboration with the University of Applied Sciences in Dresden, is highly active in the oxidation of methane and VOCs representing typical organic pollutants emitted from a wood-fired stove [14].

The aim of the present study was to prepare noble metal-doped perovskite-based monolithic catalysts and to test their activity in the oxidation of methane and selected VOCs, toluene, *n*-hexane and ethanol, differing in chemical structure. The manufactured catalysts were tested for resistance to thermal shocks and the perovskite powders were subjected to measurements of specific surface area and pore distribution.

2. METHODS

2.1. CATALYSTS PREPARATION

Five monolith-supported perovskite-based catalysts were manufactured for the study: two based on $LaMnO_3$ perovskite, one with La atoms partially substituted for silver ($La_{0.95}Ag_{0.05}MnO_3$) and two for Pt-doped perovskite ($La_{0.9}Pt_{0.1}MnO_3$, $La_{0.8}Pt_{0.2}MnO_3$). All catalysts were prepared on monolithic supports made of 00H20J5 heat-resisting steel. The supports were washcoated with Al_2O_3 (with addition of 0.8% of La_2O_3 and 14.4% of TiO_2) by the sol-gel method. After drying and calcination, the washcoat content amounted to 2 wt.%. The perovskites were prepared from the solu-

tion of $La(NO_3)_3$, $Mn(NO_3)_2$, $AgNO_3$ or H_2PtCl_6. After careful mixing, the precursors were dried at 120 °C and calcined: at 750 °C for 6 h (PER1 and Pt-doped perovskites) or at 700 °C for 8 h (PER2 and Ag-doped perovskites), and ground to the diameter of 0.07 mm. The active phase was deposited onto the washcoated support by immersion in a slurry of adequate perovskite. The characteristics of catalysts and perovskite powders are given in table 1.

Table 1

Characterization of catalysts and perovskite powders

Symbol	Type of active phase	Content of active phase (wt.%)	Calcination temperature (°C)	Calcination time (h)	SSA (m^2/g)	Micropore surface area (m^2/g)
PER1	$LaMnO_3$	14.6	700	8	14.2	0.95
PER2	$LaMnO_3$	17.8	750	6	11.6	–
PAg	$La_{0.95}Ag_{0.05}MnO_3$	13.9	700	8	13.66	1.77
PPt1	$La_{0.9}Pt_{0.1}MnO_3$	11.2	750	6	3.39	0.84
PPt2	$La_{0.8}Pt_{0.2}MnO_3$	12.2	750	6	3.1	0.32

2.2. EXPERIMENTAL METHODS

The BET specific surface area (SSA) of the perovskite powders was measured from the nitrogen adsorption isotherm by the static volumetric method at the temperature of liquid nitrogen. Based on the nitrogen adsorption isotherm, microporosity (de Boer method) and pore distribution of perovskites (Barret, Joyner and Halenda method) were determined.

The catalysts were also tested for resistance to thermal shocks by subjecting them to 4000 cycles of rapid heating up to 1000 °C and cooling down to room temperature. The heat resistance of the catalysts was expressed in terms of relative catalyst mass change after a certain number of heating and cooling cycles.

Catalyst activity tests involved combustion of methane and typical VOCs, i.e., toluene, *n*-hexane and ethanol. The process was carried out in an electrically heated quarz-glass flow reactor. The reaction temperature, measured inside the catalyst block, varied from 350 to 750 °C and from 150 to 500 °C for methane and VOCs, respectively. Methane concentration was 1 vol.% and that of each of the VOCs – 1 g/m^3. Gas hourly space velocity (GHSV) amounted to 5800 and 10000 h^{-1} for methane and VOCs, respectively. Methane concentration was measured with a Sniffer methane analyzer (Bacharach). The concentration of VOCs, as well as that of potential reaction by-products, was analyzed by gas chromatograph, using Perkin-Elmer GC, with FID, a column of 1.8 m/2.7 mm packed with 10% PEG 2000 on Chromosorb W, at a column temperature of

73 °C and an injector and detector temeprature of 100 °C.

3. RESULTS AND DISCUSSION

3.1. CATALYST STRUCTURE

Nitrogen adsorption and desorption curves as well as the pore distributions of the LaMnO$_3$, La$_{0.95}$Ag$_{0.05}$MnO$_3$ and La$_{0.9}$Pt$_{0.1}$MnO$_3$ perovskites are plotted in figure 1.
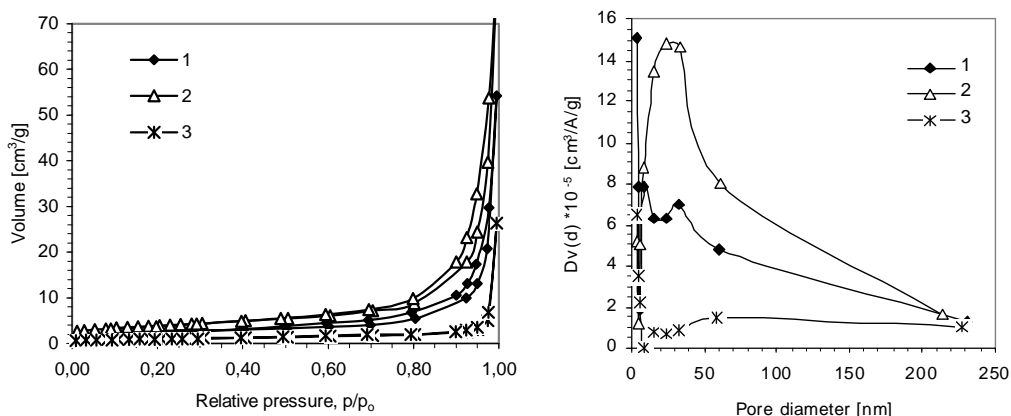

Fig. 1. Curves of nitrogen adsorption and desorption for perovskite powders (left-hand side) and pore distribution (right-hand side): 1 – LaMnO$_3$; 2 – La$_{0.95}$Ag$_{0.05}$MnO$_3$; 3 – La$_{0.9}$Pt$_{0.1}$MnO$_3$

All the samples examined are represented by an isotherm of type IV in the classification of Brunauer, Deming, Deming and Teller, and a small hysteresis loop which was similar for each catalyst. Such a small hysteresis loop indicates that the pores have the shape of a bottle with a wide inlet. The analysis of pore distribution showed a shift of LaMnO$_3$ and La$_{0.95}$Ag$_{0.05}$MnO$_3$ porosity towards the mesopore region with a similar pore diameter, i.e., 30–35 nm LaMnO$_3$ contains also micopores of 9 nm. The pore distribution of the Pt-doped perovskite differed from those of LaMnO$_3$ and La$_{0.95}$Ag$_{0.05}$MnO$_3$ in that the diameter of the pores was diverse, amouting to 15 and 60 nm.

3.2. THERMAL STABILITY OF CATALYSTS

The results of thermal shock resistance measurements are presented in figure 2.
Both perovskite-based catalysts showed a higher resistance to thermal shock than

those doped with Ag or Pt. Partial substitution of La for Ag (0.05 mol) in the $LaMnO_3$ structure reduced the thermal resistance of the catalyst. Initially, after 500 cycles, the relative mass loss was greater for the Ag-doped catalyst than for the PER2 one. However, after subsequent 4000 heating and cooling cycles, a relative loss of mass was nearly the same for both catalysts, amounting to 3.5 and 3%, respectively. Generally, the thermal resistance of the catalysts calcined at 750 °C (PER1 and Pt-containing perovskites) was higher than that of the catalysts calcined at 700 °C, and the relative loss of mass after 4000 cycles of thermal shocks amounted to only 0.7% for PER1 and 1.15% for both the Pt-doped catalysts (figure 2).
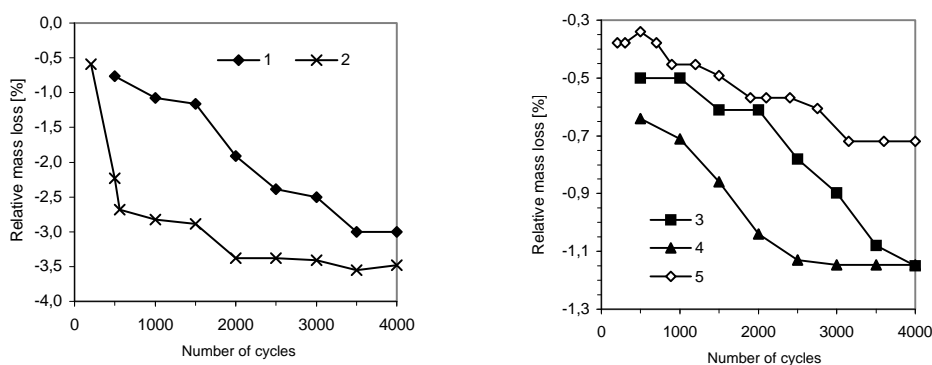

Fig. 2. Thermal resistance of perovskite alone and Ag-containing catalysts (left-hand side):
1 – PER1; 2 – $La_{0.95}Ag_{0.05}MnO_3$; and Pt-containing catalysts (right-hand side);
3 – $La_{0.9}Pt_{0.1}MnO_3$; 4 – $La_{0.8}Pt_{0.2}MnO_3$; 5 – PER2

3.3. CATALYST ACTIVITY IN METHANE AND VOC COMBUSTION

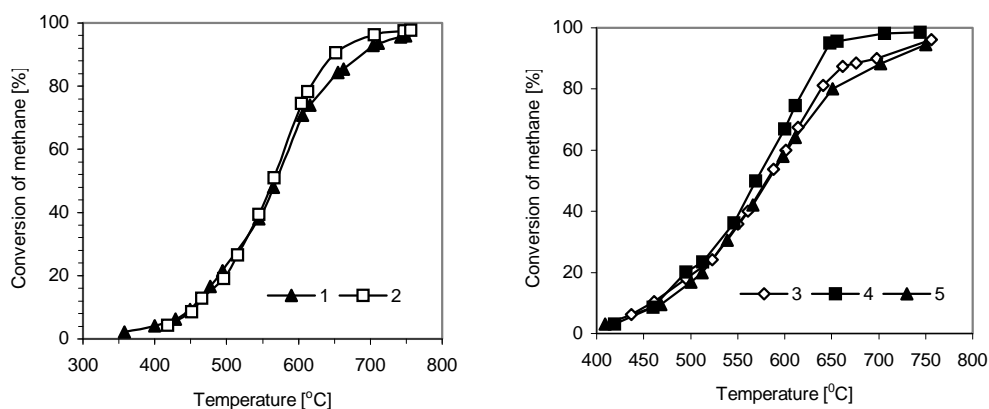The results of methane combustion over the catalysts tested are shown in figure 3.

Fig. 3. Methane conversion over PER 1 and Ag-containing catalysts (left-hand side):
1 – $La_{0.95}Ag_{0.05}MnO_3$; 2 – PER 1; and over PER 2 and Pt-containing catalysts (right-hand side);
3 – PER 2; 4 – $La_{0.9}Pt_{0.1}MnO_3$; 5 – $La_{0.8}Pt_{0.2}MnO_3$

The activity of the catalysts in methane combustion depended on both the temperature of catalyst calcination and the amount of noble metal added. Irrespective of the preparation method used and noble metal added, the temperature of 50% methane conversion was 570 °C for all the catalysts. At higher reaction temperatures, catalytic activity depended on the temperature of calcination. Higher activity was observed with catalysts calcined at 700 °C, and the temperature for 90% methane combustion reached 650 and 700 °C for PER1 and PER2, respectively (figure 3). The incorporation of Ag decreased the activity of the catalyst, hence in order to achieve 90% methane conversion over $La_{0.95}Ag_{0.05}MnO_3$ it was necessary to apply a temperature by 40 °C higher. The highest activity in methane combustion was found to be that of $La_{0.9}Pt_{0.1}MnO_3$, and 90% methane combustion over this catalyst was observed at 630 °C only. The increase in Pt content to 0.2 mol decreased the catalyst activity, the temperature of 90% methane conversion amounting to 720 °C.
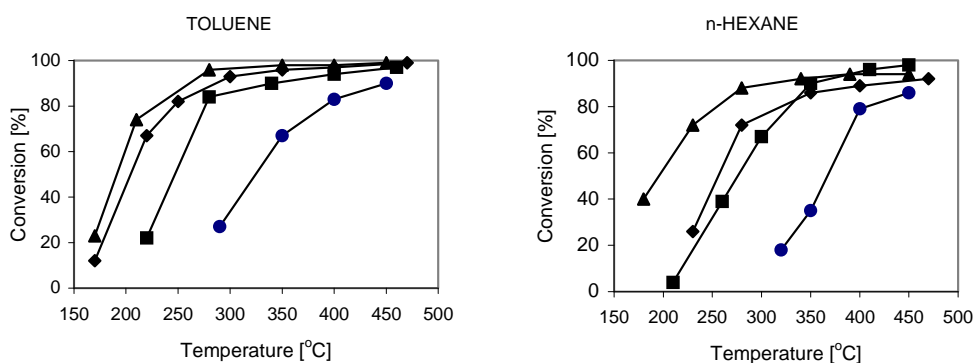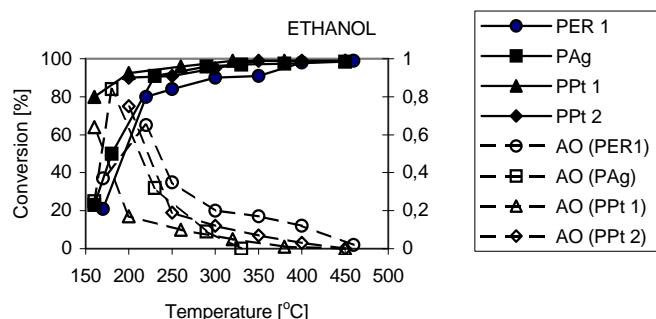
Fig. 4. VOC conversion and concentration of acetaldehyde (AO),
the product of incomplete ethanol oxidation, detected in reaction gas [g/m^3]

The results of VOC conversion are plotted in figure 4. The temperatures of 50% and 90% conversion of the compounds tested are shown in table 2.

Table 2

Temperatures (in °C) of 50% and 90% conversion of oxidized VOCs

Catalyst	Toluene		*n*-Hexane		Ethanol	
	50%	90%	50%	90%	50%	90%
PER1	325	450	365	>450	215	300
PAg	245	340	275	350	180	225
PPt1	190	260	195	300	160	200
PPt2	205	275	255	400	<160	200

The catalyst based on LaMnO$_3$ alone showed the lowest activity in the oxidation of all the VOCs tested at the temperatures of 50% conversion amounting to 325, 365 and 215 °C for toluene, *n*-hexane and ethanol, respectively. 90% toluene and ethanol oxidation was achieved at 450 and 300 °C, respectively, while at the highest temperature tested, i.e. 450 °C, *n*-hexane conversion reached 86%.

A small (0.05 mol) addition of silver to the LaMnO$_3$ phase (La$_{0.95}$Ag$_{0.05}$MnO$_3$) sufficed to increase the catalyst activity. The temperatures needed for 50% conversion of toluene, *n*-hexane and ethanol were by 80, 90 and 35 deg lower than that for PER1; the temperatures of 90% conversion amounting to 340, 350 and 225 °C, respectively.

The incorporation of Pt into LaMnO$_3$ distinctly improved the activity of the latter. But catalytic activity was found to be higher for PPt1 with a lower Pt content (0.1 mol). 50% toluene and *n*-hexane conversion was achieved at 190–195 °C. At the lowest temperature investigated, i.e., 160 °C, ethanol conversion reached 80%. Over this catalyst, 90% conversion of each oxidized VOC was achieved at the lowest temperatures compared with the other catalysts (table 2). The Pt content of 0.2 mol did not

enhance the catalyst activity. Moreover, in *n*-hexane oxidation the activity of PPt2 was distinctly lower than that of PPt1 and was also lower in methane oxidation. This implies that the catalyst with the higher platinum content was possibly deactivated by the chlorine which originated from the Cl-containing Pt precursor (H_2PtCl_6) [15].

The reaction of ethanol oxidation ran via the production of acetaldehyde (AA) detected in the flue gas. The concentration of aldehyde greatly depended on the catalyst activity in ethanol combustion. Over the most active PPt1 catalyst, at 200 °C which is the temperature of 90% ethanol conversion, the concentration of AA reached 0.18 g/m^3. In the presence of the less active catalysts, aldehyde was detected even at high reaction temperatures.

4. CONCLUSIONS

Partial substitution of lanthanum for silver (0.05 mol) in the $LaMnO_3$ active phase improved catalyst activity in the oxidation of the VOCs, but did not influence catalytic activity in the process of methane combustion.

The incorporation of platinum (0.1 mol) into $LaMnO_3$ enhanced the catalyst activity in the oxidation of both methane and VOCs. Further increase in platinum content did not improve catalytic properties, but it reduced the activity of the catalyst in methane and *n*-hexane oxidation. This effect may be attributed to the deactivation of the catalyst by the chlorine ions originating from the Cl-containing platinum precursor (H_2PtCl_6). To prove this further investigations into the preparation of catalysts using a Pt-precursor other than H_2PtCl_6, for example $Pt(NO_3)_4$, are necessary.

The high activity of the $La_{0.9}Pt_{0.1}MnO_3$ catalyst may be due to the diversity of its pore distribution, despite a small specific surface area. The analysis of pore distribution showed a high proportion of pores both 15 and 60 nm in diameter. As for the other catalysts, the pores of 30–35 nm diameters prevailed.

Doping the catalysts with Ag or Pt slightly decreased their resistance to thermal shocks.

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UTLENIANIE ORGANICZNYCH ZANIECZYSZCZEŃ POWIETRZA NA MONOLITYCZNYCH KATALIZATORACH PEROWSKITOWYCH ZMODYFIKOWANYCH METALAMI SZLACHETNYMI

Wykonano pięć katalizatorów na monolitycznym nośniku metalicznym. Ich czynnikiem aktywnym był perowskit $LaMnO_3$ sam i z lantanem częściowo zastąpionym srebrem ($La_{0.95}Ag_{0.05}MnO_3$) lub platyną ($La_{0.9}Pt_{0.1}MnO_3$, $La_{0.8}Pt_{0.2}MnO_3$). Aktywność tych katalizatorów przebadano, utleniając w ich obecności metan oraz pary toluenu, *n*-heksanu i etanolu. Najwyższą aktywność wykazał katalizator z perowskitem $La_{0.9}Pt_{0.1}MnO_3$, choć jego powierzchnia właściwa była bardzo mała (3.39 m^2/g). W tym perowskicie stwierdzono znaczny udział porów o średnicy 15 i 60 nm, w pozostałych perowskitach przeważały pory o średnicy 30–35 nm. Wszystkie katalizatory z dodatkiem metali szlachetnych charakteryzowały się nieco niższą odpornością na szoki termiczne niż katalizatory na bazie samego $LaMnO_3$.