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Catalytic Oxidation of Carbon Monoxide on Pd-Containing $LaMnO_3$ Perovskites

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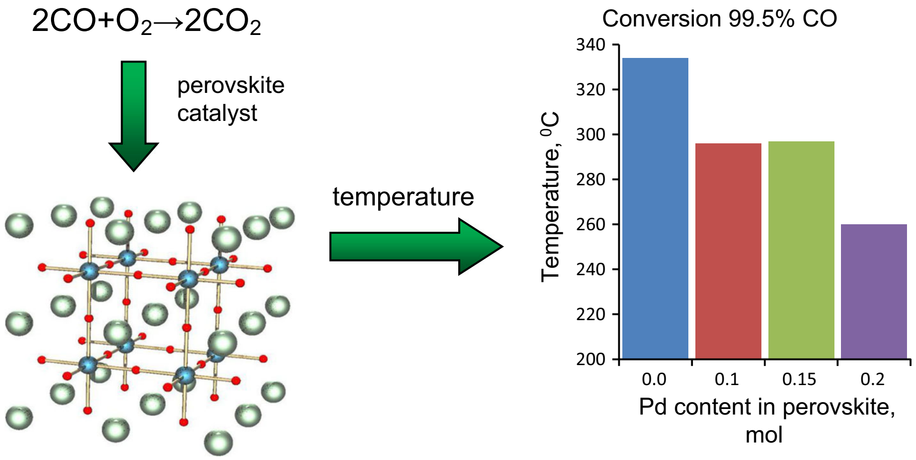
Abstract The substitution of 0.05 mol La with Pd enhances the activity of the $LaMnO_3$ in CO oxidation. $La_{0.9}Pd_{0.1}MnO_3$ and $La_{0.85}Pd_{0.15}MnO_3$ catalysts exhibit a very high activity, which depends on the conditions of perovskite preparation. Monolithic catalysts display a higher activity during CO oxidation when based on $La_{1-x}Pd_xMnO_3$ than $LaMn_{1-x}Pd_xO_3$ perovskites. The activity of the catalysts is determined by the concentration of palladium on the catalyst surface, which increases as the precursor calcination temperature is raised from 650 to 800 °C. The size of the specific surface area of the perovskites has smaller influence on the activity of the catalysts.

Graphical Abstract



Keywords Environmental catalysis · Perovskite · CO oxidation · Monolithic catalyst

1 Introduction

Perovskite catalysts ABO_3 A=La, Sr, Ce, Nd, Sm, and B=Co, Mn, Cr, Fe, Ni show high activity for CO and hydrocarbons oxidation and high thermal resistance [1–21].

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The activity of the perovskite in oxidation processes can be enhanced by partial substitution of the metal in position A and/or position B with metal cations differing in their valence number. Such substitution changes the properties of the perovskite by inducing structural and electronic defects, which contribute to the perovskite's non-stoichiometry and thus considerably improve its catalytic activity [2, 4]. The catalytic properties of the perovskite can be improved by partial substitution of the metal in position A or B with cations of noble metals: silver [3, 5], platinum [6, 7] or palladium [8–21]. The activity of perovskites for the oxidation of hydrocarbons and CO can be enhanced either by partial substitution of palladium for the metal in position B ($LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$, $LaB_{0.95}Pd_{0.05}O_3$ B=Mn, Fe, Co, Ni) or by depositing palladium on the surface of the perovskite ($Pd/La_{0.9}Ce_{0.1}Co_{0.4}Fe_{0.6}O_3$, $Pd/LaFe_{0.8}Co_{0.2}O_3$) [8–10]. When deposited onto $La_{0.9}Ce_{0.1}Co_{1-x}Fe_xO_3$ perovskites, palladium is the dominant contributing factor in the catalyst's activity, which, however, is also influenced by the type of the perovskite used [9]. The activity of a three-way automotive exhaust catalyst with the same palladium loading is significantly higher with Pd deposited on the $LaFe_{0.8}Co_{0.2}O_3$ perovskite-type oxide than with Pd substituted for iron in the $LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$ perovskite [9].

The activity of Pd-doped perovskites is strongly influenced by the method of their preparation [11].

In Pd-containing perovskite-type oxides ($LaBO_3$ B=Fe, Co) a solid solution of Pd forms in the crystals the formation of which was affected by the metals in position B. In the $LaFe_{0.54}Co_{0.36}Pd_{0.1}O_3$ perovskite palladium is more durable than in $LaCo_{0.9}Pd_{0.1}O_3$ and $LaFe_{0.9}Pd_{0.1}O_3$ [12]. Owing to the strong palladium–perovskite interaction, thermal ageing at a high temperature does not induce sintering or crystal growth in the $LaFe_{0.54}Co_{0.36}Pd_{0.1}O_3$ perovskite. $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ [13], $LaFe_{0.95}Pd_{0.05}O_3$ [6] and $LaCo_{0.95}Pd_{0.05}O_3$ [14] perovskites have been used as three-way automotive exhaust catalysts. In fresh perovskites Pd is incorporated into the metal in position B; during reduction palladium segregates from the perovskite lattice and disperses in the form of metallic Pd nanoparticles on the catalyst surface. At alternating variations in atmosphere from oxidizing to reducing Pd reversibly enters and leaves the perovskite lattice, which prevents crystal growth in metallic Pd and thus enables the high catalytic activity to be maintained for a long time, also after ageing. It has been reported that the $LaCo_{0.95}Pd_{0.05}O_3$ catalyst is the most active upon 30-min reduction at 180 °C [14]. Under reaction conditions the activity of $LaCo_{0.95}Pd_{0.05}O_3$ and $LaFe_{0.95}Pd_{0.05}O_3$ catalysts for CO oxidation does not decrease during 660-min ageing at 850 °C [14] and 100-h ageing at 900 °C [6], respectively.

As three-way catalysts, the Pd-containing $La_{0.91}Mn_{0.85}Ce_{0.24}Pd_{0.05}O_z$ and $La_{1.034}Mn_{0.966}Pd_{0.05}O_z$ perovskites exhibit high activity for CO, CH_4 and NO_x removal. Their activation through high-temperature hydrothermal treatment has disclosed the migration of Pd out of the perovskite lattice and the formation of segregated PdO. Low Pd content causes more dispersion of oxidized Pd^{n+} ($n = 2$–4) and enhances catalytic activity [15].

Although the activity of perovskite catalysts in CO oxidation is lower than that of conventional catalysts made of noble metals (Pt, Pd), they have other advantages, such as: higher sulphur tolerance and improved activity in the presence of water vapour. The introduction of a noble metal into a perovskite prevents the sintering of the latter and a reduction in its mass as a result of volatilization at a high temperature in oxidizing conditions [16].

The aim of the present study was to examine how the substitution of palladium for some of the lanthanum or manganese in the $LaMnO_3$ perovskite, and the mode of perovskite preparation influence the activity of $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-y}Pd_yO_3$ for CO oxidation. The physicochemical properties of the perovskites were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET specific surface area (SSA) measurement.

2 Experimental

2.1 Catalysts Preparation

Monolithic perovskite catalysts were supported on heat-resisting FeCr20 %Al5 % foil (Sandvik). The support, a 70 mm high, 26 mm diameter cylinder of a honeycomb cross-section with triangular channels, was washcoated with 99.31 $\%Al_2O_3$–0.59 $\%TiO_2$–0.1 $\%La_2O_3$ (2 ± 0.1 wt%) by the sol–gel method. The active phase was composed of perovskite-type oxides: $LaMnO_3$, $La_{1-x}Pd_xMnO_3$ $x = 0.05$–0.2 and $LaMn_{1-y}Pd_yO_3$ $x = 0.1$–0.15. Perovskites were prepared by dissolving appropriate quantities of $La(NO_3)_3{\cdot}6H_2O$ (analytically pure, Fluka), $Mn(NO_3)_2{\cdot}4H_2O$ (analytically pure, Merck) and $Pd(NO_3)_2$ (Mint of Poland) in distilled water, followed by drying at 120 °C and calcination at 650–850 °C. The perovskite obtained was ground and sieved to the size of 0.07 mm. The active layer was deposited by immersion of the support in the suspension of an appropriate perovskite in citric acid solution. The catalysts were calcined for 3 h at 500 °C in air. The amount of the deposited active layer averaged 11.5 wt% ($LaMnO_3$), 12.5 wt% ($La_{1-x}Pd_xMnO_3$) and 13.5 wt% ($LaMn_{1-x}Pd_xO_3$). The perovskite-based catalysts are characterized in Table 1.

Table 1 Preparation parameters and characterization of the perovskite powders

The stoichiometric composition of perovskites	Calcination temperature (°C)	Calcination time (h)	Pd content (wt%)	SSA of perovskite powders ($m^2\ g^{-1}$)	Pd/(Pd + Mn + La) (XPS)
$LaMnO_3$	750	6	0	8.6	0
$La_{0.95}Pd_{0.05}MnO_3$	750	6	2.21	10.6	–
$La_{0.9}Pd_{0.1}MnO_3$	750	6	4.46	9.4	–
$La_{0.8}Pd_{0.2}MnO_3$	750	6	9.04	9.4	–
$La_{0.85}Pd_{0.15}MnO_3$	650	8	6.73	12.3	0.016
$La_{0.85}Pd_{0.15}MnO_3$	750	6	6.73	8.8	0.034
$La_{0.85}Pd_{0.15}MnO_3$	800	4	6.73	6.1	0.046
$La_{0.85}Pd_{0.15}MnO_3$	850	4	6.73	3.5	0.034
$LaMn_{0.9}Pd_{0.1}O_3$	750	6	4.30	8.3	–
$LaMn_{0.9}Pd_{0.1}O_3$	800	4	4.30	6.3	–
$LaMn_{0.85}Pd_{0.15}O_3$	650	8	6.39	10.9	0.009
$LaMn_{0.85}Pd_{0.15}O_3$	750	6	6.39	9.0	0.021
$LaMn_{0.85}Pd_{0.15}O_3$	800	4	6.39	6.9	0.056
$LaMn_{0.85}Pd_{0.15}O_3$	850	4	6.39	4.7	0.048

2.2 Catalysts Characterization

Phase composition was examined by XRD using a Philips Materials research diffractometer. Measurements were performed in parallel beam optics. The active layer was illuminated at a constant angle ($\omega = 5°$), the scan being 2Θ.

The surface of the catalysts was examined by SEM, using a JSM 6800LV instrument (made by Jeol), equipped with an ISIS 300 Oxford microanalysis system (EDS).

BET SSA were calculated from nitrogen sorption isotherms measured by the static volumetric method at the temperature of liquid nitrogen, using an Autosorb-1-C/TCD instrument. Adsorption measurements were carried out with outgassed (at 150 °C) catalyst samples until the pressure rise limit was equal to, or lower than, 20 μmHg min^{-1}.

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

2.3 Catalytic Activity

Catalytic activity was tested in the oxidation of 1 % CO in air. The monolithic catalysts were placed in a quartz flow reactor heated with an electrical tubular furnace (heating ramp 3 °C min^{-1}). Catalyst temperature was measured with a K-type thermocouple in a monolith channel 15 mm from the gas exit. Oxidation of CO was examined over the temperature range of 120–400 °C, gas hourly space velocity (GHSV) being set to 10,000 h^{-1} based on fully monolith support volume (26,560 h^{-1} based on empty monolith support volume). The volume of voids in the monolith is 0.0226 dm^3 and the gas flow rate is 350 $dm^3\ h^{-1}$. The time of gas contact with the monolith is 0.23 s.

CO concentrations were determined using a Monoxor II analyzer (Bacharach) (measuring range 1–1999 ppm) and an automotive emission analyzer MEXA-574GE (Horiba) (measuring range 0.01–10.00 %), the accuracy of the analyzers being ±5 % of the measured value.

3 Results and Discussion

XRD patterns for catalysts containing fresh $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskite-type oxides calcined at 750 °C for 6 h revealed the presence of the $LaMnO_{3.1}$ phase and metallic Pd; there are also visible peaks of Fe–Cr coming from the heat-resisting foil of which the support was made (Fig. 1). XPS analyses showed the maximum of the Pd $3d_{5/2}$ peak on the surface of the $La_{0.85}Pd_{0.15}MnO_3$ catalyst at approx. 336.5 eV and the half-intensity widths (FWHM) value was found to be below 1.9 eV [17]. This peak can be ascribed to PdO. The different results yielded by XRD and XPS indicate that under such calcination conditions Pd^{2+} undergoes reduction and segregates, in the form of Pd^0, to the perovskite's surface. Pd^0 superficially oxidizes to PdO (XPS) and is present on the perovskite's surface as metallic palladium coated with PdO (PdO/Pd^0).

The XRD patterns of monolithic catalysts with $LaMn_{1-x}Pd_xO_3$ x = 0.1 and 0.15 perovskites calcined at 800 and 850 °C for 4 h display the $LaMnO_{3.1}$ phase, PdO and Fe–Cr peaks. On the surface of the catalysts which

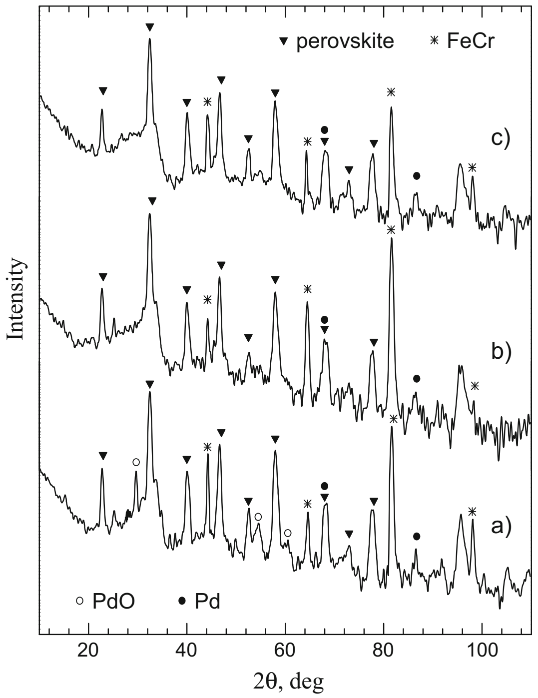

Fig. 1 XRD patterns of fresh monolithic $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ catalysts: *a* $La_{0.85}Pd_{0.15}MnO_3$ (calcined at 800 °C for 4 h); *b* $La_{0.85}Pd_{0.15}MnO_3$ (calcined at 750 °C for 6 h); *c* $LaMn_{0.85}Pd_{0.15}O_3$ (calcined at 750 °C for 6 h)

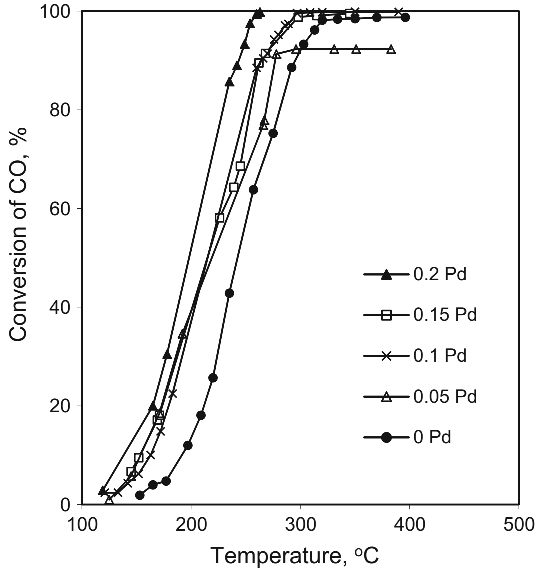

Fig. 2 CO conversion over monolithic $La_{1-x}Pd_xMnO_3$ catalysts as a function of Pd content (x). Perovskite powders calcined at 750 °C for 6 h

contain $LaMn_{0.85}Pd_{0.15}O_3$ palladium occurs in different oxidation states as: Pd^0, Pd^{+2}, Pd^{+3} and Pd^{+4} and higher FWHM values are observed (>2.2 eV) (XPS) [17].

It was found that the SSA of perovskite-type oxides $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ decreased when the calcination temperature of their precursors was raised from 650 to 850 °C, despite the reduced calcination time. Thus, when calcination temperature increased from 650 to 850 °C, the SSA value decreased from 12.3 to 3.5 $m^2\ g^{-1}$ for $La_{0.85}Pd_{0.15}MnO_3$, and from 10.9 to 4.7 $m^2\ g^{-1}$ for $LaMn_{0.85}Pd_{0.15}O_3$. In the case of $La_{1-x}Pd_xMnO_3$ ($x = 0.05$–0.2) perovskite-type oxides calcined in the same conditions, the influence of their Pd content on the SSA was confirmed. At 750 °C, their SSA value fell from 10.6 to 9.4 $m^2\ g^{-1}$ when the Pd content increased from 0.05 to 0.2 mol (Table 1). For $LaMn_{1-x}Pd_xO_3$ perovskites, at the calcination temperature of 750 °C the increase in Pd content from 0.1 to 0.15 mol brought about a slight increase in their SSA values (8.3 and 9.0 $m^2\ g^{-1}$, respectively). When $LaMn_{1-x}Pd_xO_3$ $x = 0.1$–0.15 perovskites were calcined at 800 °C, their SSA values did not change with Pd content (about 6.9 $m^2\ g^{-1}$). The SSA values of the perovskites described in this paper are close to the ones obtained by other authors [10, 11]. However, the SSA value of a perovskite depends on the preparation method. For example, the SSA value of the $LaMn_{0.95}Pd_{0.05}O_3$ perovskite obtained by the method described in this paper amounts to 10.6 $m^2\ g^{-1}$ (calcination at 750 °C). A similar SSA value (12 $m^2\ g^{-1}$) was obtained for this perovskite by Lu et al. [11] who used the citric acid method (calcination at 700 °C). The same perovskite obtained through solution combustion synthesis (SCS) had the SSA value of 8.0 $m^2\ g^{-1}$ [10] or 1 $m^2\ g^{-1}$ [11]. Much higher SSA values of the perovskite were obtained by Lu et al. when they used ultrasonic spray combustion (39 $m^2\ g^{-1}$) and flame spray synthesis (32 $m^2\ g^{-1}$) [11].

In the case of perovskites obtained by the 6-h calcination of metal nitrates at 750 °C, the conversion of CO increased when Pd content was raised from 0.05 to 0.2 mol (Fig. 2). However, the substitution of palladium for 0.05 mol of lanthanum ($La_{0.95}Pd_{0.05}MnO_3$) sufficed to noticeably enhance the activity of $LaMnO_3$ for CO oxidation, causing a reduction in CO oxidation temperatures T_{10}, T_{50} and T_{90} by 32, 20 and 25 °C. The enhancement (observed in spite of the decrease in the SSA of $La_{1-x}Pd_xMnO_3$ perovskites with the rise in their Pd content) (Table 1) should be attributed to the increased content of palladium, whose activity in CO oxidation is markedly higher than that of the $LaMnO_3$ perovskite. The highest activity in CO oxidation was found to be that of the $La_{0.8}Pd_{0.2}MnO_3$-based catalyst. Catalysts based on $La_{0.85}Pd_{0.15}MnO_3$ and $La_{0.9}Pd_{0.1}MnO_3$ perovskites exhibit high CO oxidation activities. Temperatures T_{10}, T_{50} and T_{90} for these catalysts are only by 12 °C higher than the ones obtained for the $La_{0.8}Pd_{0.2}MnO_3$ catalyst (Table 2).

The activity of monolithic $La_{1-x}Pd_xMnO_3$ catalysts for CO oxidation depends on the temperature and time of

Table 2 Comparison of carbon oxide oxidation over monolithic catalysts with $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ as active phase

Composition of active phase	Calcination temperature (°C)	Catalytic activity in terms of conversion temperature (°C)		
		T_{10}	T_{50}	T_{90}
$LaMnO_3$	750	195	240	295
$La_{0.95}Pd_{0.05}MnO_3$	750	163	220	270
$La_{0.9}Pd_{0.1}MnO_3$	750	163	215	265
$La_{0.85}Pd_{0.15}MnO_3$	750	152	212	263
$La_{0.8}Pd_{0.2}MnO_3$	750	140	200	250
$La_{0.85}Pd_{0.15}MnO_3$	650	165	212	260
$La_{0.85}Pd_{0.15}MnO_3$	800	<130	183	250
$La_{0.85}Pd_{0.15}MnO_3$	850	165	220	260
$LaMn_{0.9}Pd_{0.1}O_3$	750	172	213	268
$LaMn_{0.9}Pd_{0.1}O_3$	800	169	219	262
$LaMn_{0.85}Pd_{0.15}O_3$	650	180	240	300
$LaMn_{0.85}Pd_{0.15}O_3$	750	180	232	275
$LaMn_{0.85}Pd_{0.15}O_3$	800	175	222	270
$LaMn_{0.85}Pd_{0.15}O_3$	850	160	208	258

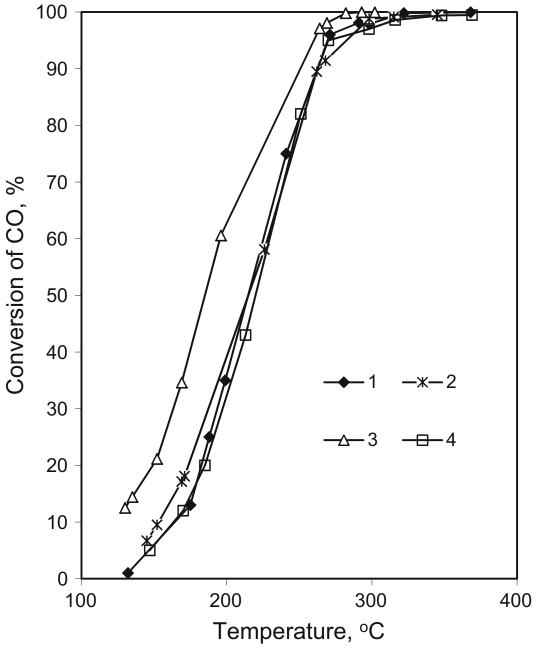

Fig. 3 CO conversion over monolithic $La_{0.85}Pd_{0.15}MnO_3$ catalysts as a function of perovskite calcination temperature. Perovskite powders calcined at 650 °C for 8 h (*1*); at 750 °C for 6 h (*2*); at 800 °C for 4 h (*3*), and at 850 °C for 4 h (*4*)

perovskite calcination. $La_{0.85}Pd_{0.15}MnO_3$ catalysts with perovskites calcined at 650, 750 and 850 °C exhibit similar CO oxidation activities (Fig. 3). Among them the one with the perovskite obtained by the 4-h calcination of lanthanum, manganese and palladium nitrates at 800 °C is the most active, which can be ascribed to the presence not only of the $LaMnO_{3.1}$ phase but also of PdO segregating to the surface of the perovskite (Fig. 1), which displays high activity in oxidation processes. The rise in calcination temperature from 800 to 850 °C noticeably reduced the SSA of the $La_{0.85}Pd_{0.15}MnO_3$ perovskite (from 6.1 to 3.5 $m^2\ g^{-1}$), and the activity of the catalyst decreased considerably despite the presence of PdO. The rise in calcination temperature from 750 °C (6 h) to 800 °C (4 h) was concomitant with a noticeable increase in the catalytic activity of $La_{0.95}Pd_{0.05}MnO_3$. Thus, the optimal conditions for preparing $La_xPd_{1-x}MnO_3$ perovskites include the 4-h calcination of a mixture of appropriate nitrates at 800 °C (Table 2).

CO oxidation tests were also conducted to examine the activities of catalysts based on $LaMn_{0.9}Pd_{0.1}O_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskite-type oxides, where palladium was substituted for some of the manganese. The activity of the $LaMn_{0.85}Pd_{0.15}O_3$ catalyst with palladium substituted for 0.15 mol of manganese largely depended on the conditions of perovskite preparation, and was found to increase with the rise in calcination temperature from 650 to 850 °C and with the decrease in calcination time from 8 to 4 h. In the case of the catalyst with the $LaMn_{0.85}Pd_{0.15}O_3$ perovskite calcined at 850 °C for 4 h, 90 % conversion of CO was reached at 258 °C (Table 2). Despite the lowest SSA of the $LaMn_{0.85}Pd_{0.15}O_3$ perovskite (Table 1) obtained when the precursors were calcined at 850 °C, catalysts with such perovskites show higher CO oxidation activity than the perovskites calcined at 750–800 °C (Fig. 4). When in the $LaMnO_3$ perovskite palladium was substituted for 0.1 mol of manganese ($LaMn_{0.9}Pd_{0.1}O_3$), the rise in

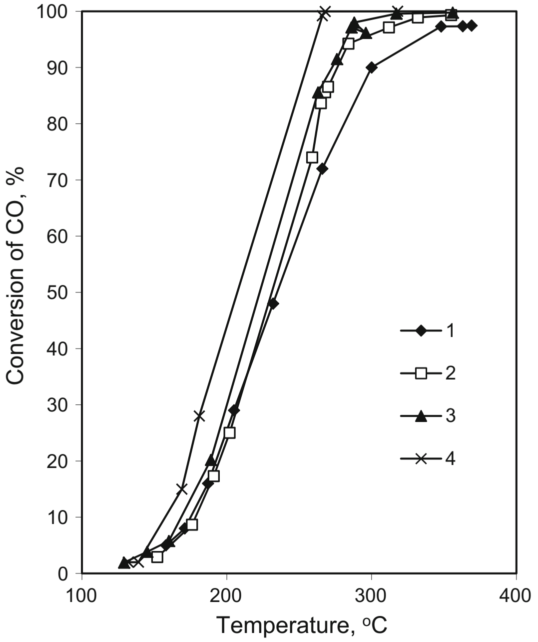

Fig. 4 CO conversion over monolithic $LaMn_{0.85}Pd_{0.15}O_3$ catalysts as a function of perovskite calcination temperature. Perovskite powders calcined at 650 °C for 8 h (*1*); at 750 °C for 6 h (*2*); at 800 °C for 4 h (*3*), and at 850 °C for 4 h (*4*)

calcination temperature from 750 to 800 °C only slightly affected the activity of the catalyst during CO oxidation (Table 2). The results show that the SSA of the perovskite has little influence on the activity of the monolithic catalysts with perovskites $LaMn_{1-x}Pd_xO_3$ x = 0.1, 0.15.

For all the catalysts with the $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ perovskites containing Pd temperatures T_{10}, T_{50} and T_{90} in CO oxidation are lower than for the catalyst with $LaMnO_3$ (Table 2). This proves that the activity of the catalyst with the $LaMnO_3$ perovskite increased after palladium was introduced into it.

A comparative analysis of $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ perovskites activity for CO oxidation revealed that even if Pd contents (x) and preparation conditions are the same (calcination at 650 to 800 °C), $La_{1-x}Pd_xMnO_3$ perovskites are more active (Table 2). For $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskite powders (calcination at 750 °C for 6 h) the SSA values were similar (8.8 and 9 $m^2\ g^{-1}$, respectively). However, from the SEM images it is seen that the crystallites occurring on the surface of the $LaMn_{0.85}Pd_{0.15}O_3$ catalyst are a little larger than the ones on the surface of the $La_{0.85}Pd_{0.15}MnO_3$ catalyst (Fig. 5).

A previous study [17] demonstrated that on the surface of $La_{1-x}Pd_xMnO_3$ catalysts palladium occurs mainly in the form of PdO and in $La_{1-x}Pd_xMnO_3$ perovskites a greater amount of palladium segregates to the surface than in $LaMn_{1-x}Pd_xO_3$ perovskites (XPS). The values of the Pd/(Pd + La + Mn) ratios calculated from XPS patterns are 0.009 (calcination at 650 °C) and 0.021 (calcination at 750 °C) for the $LaMn_{0.85}Pd_{0.15}O_3$ perovskite; those for the $La_{0.85}Pd_{0.15}MnO_3$ perovskite amount to 0.016 and 0.034, respectively (Table 1). On the basis of the X-ray

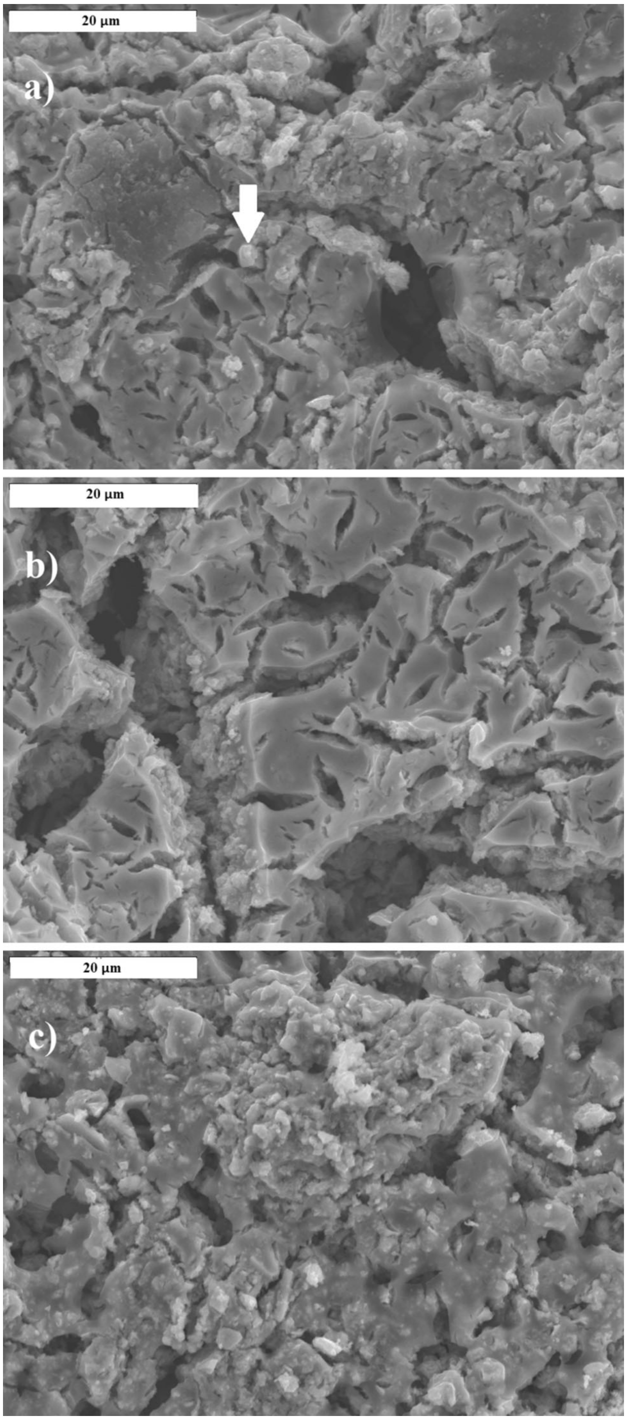

Fig. 5 SEM images of the surfaces of the $La_{0,85}Pd_{0,15}MnO_3$ (calcined at 750 °C for 6 h) (**a**), $LaMn_{0,85}Pd_{0,15}O_3$ (calcined at 750 °C for 6 h) (**b**) and $La_{0,85}Pd_{0,15}MnO_3$ (calcined at 800° for 4 h) perovskite-based monolithic catalysts

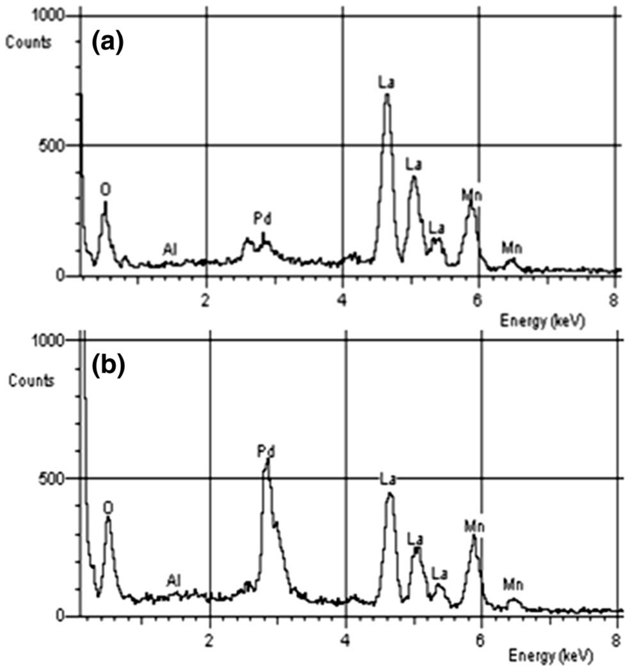

Fig. 6 X-ray microanalysis (EDS) $La_{0.85}Pd_{0.15}MnO_3$ catalyst. EDS analysis of: the catalyst surface (**a**), analysis of Pd-containing crystallite (indicated with an *arrow* on Fig. 5a) (**b**). Perovskite powders calcined at 750 °C for 6 h

microanalysis (EDS) it was calculated that the Pd/(Pd + La + Mn) ratios in the surface layer of the $LaMn_{0.85}Pd_{0.15}O_3$ and $La_{0.85}Pd_{0.15}MnO_3$ catalysts (calcination at 750 °C) are similar to the ones obtained from the XPS analysis, amounting to respectively 0.029 and 0.032. Thus, the higher CO oxidation activity of $La_{1-x}Pd_xMnO_3$ can be attributed to a larger quantity of Pd present on its surface and in the surface layer.

At the same time the X-ray microanalysis shows that on the surface of the studied catalysts there are crystallites with considerably higher palladium concentrations than the average palladium concentration in the analysed area (Fig. 6). Figure 6b shows an X-ray microanalysis (EDS) of the crystallite marked with arrow in Fig. 5a. On the basis of the X-ray microanalysis the Pd/(Pd + La + Mn) ratios in the crystallites were found to amount to 0.176 ($LaMn_{0.85}Pd_{0.15}O_3$) and 0.31 ($La_{0.85}Pd_{0.15}MnO_3$) and they are 2.35 and 4.1 higher than the stoichiometric values (0.075). The palladium crystallites on the surface of the $La_{0.85}Pd_{0.15}MnO_3$ catalyst (calcination at 750 °C) are about 0.8–2.5 µm in size (Fig. 5a). They are slightly larger than the crystallites on the $LaMn_{0.95}Pd_{0.05}O_3$ catalyst (calcination at 700 °C for 5 h) [10], whose size calculated on the basis of the BET surface area amounts to 115 nm (0.115 µm). However, the catalyst in [10] was calcined at a lower temperature and over a shorter time. A similar palladium crystallite size as after calcination at 750 °C is observed on the surface of the $La_{0.85}Pd_{0.15}MnO_3$ catalyst calcined at 800 °C, but single crystals 4–5 µm in size are also observed on this surface (Fig. 5c). Still, there are considerably more palladium crystallites on the surface of the perovskite after calcination at the temperature of 800 °C than at 750 °C (Fig. 5), which is in agreement with the XPS results, according to which as the calcination temperature is increased from 750 to 800 °C the ratio of Pd to Pd + Mn + La increases from 0.034 to 0.046 (Table 1).

The tests indicate that palladium is not uniformly distributed in the catalyst and probably it did not incorporate itself into the structure of the perovskite. After the partial substitution of lanthanum or manganese by palladium in the $LaMnO_3$ perovskites the increase in their activity in the oxidation of carbon monoxide is caused by the PdO or PdO/Pd^0 dispersed on the surface of the perovskites and depends on the palladium concentration on the catalyst surface. The results obtained in this study are in agreement with the ones reported by Eyssler et al. [21] and Lu et al. [11].

According to the literature on the subject, the incorporation of Pd into the structure of the $LaBO_3$ perovskite depends on both the kind of cation in position B of the perovskite to which Pd is introduced [10, 11, 16, 21] and the perovskite preparation method used [11]. The amount of the noble metal (Pd, Pt, Rh) which can form a solid solution with a perovskite-type oxide is different for each noble metal–perovskite combination [16]. When synthesizing $LaBPdO_3$ (B=Fe, Co, Mn) perovskites by the amorphous citrate method [21], Eyssler et al. found that Pd incorporates itself into the structures of the $LaFeO_3$ and $LaCoO_3$ perovskites, but it does not incorporate itself into the structure of the $LaMnO_3$ perovskite, being only dispersed in the form of PdO on its surface. This is connected with the size of the ionic radii of the metal in position B of the perovskite and Pd^{3+}. The smaller size of manganese does not favour the occupation of the octahedral sites by the larger Pd^{3+} [21]. This is confirmed by other studies where it is reported that Pd incorporates itself into the structure of perovskites containing Fe and/or Co as the metal in position B of the perovskite, e.g. $LaFe_{0.95}Pd_{0.05}O_3$ [6, 16, 19], $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ [13, 20] and $LaCo_{0.95}Pd_{0.05}O_3$ [14]. Also Ziaei-Azad et al. do not exclude that Pd incorporates itself into the structure of the $LaB_{0.95}Pd_{0.05}O_3$ (B=Mn, Fe, Co, Ni) perovskites, even though their XRD analyses show the presence of a small amount of a separate PdO phase [10]. Katz et al. maintain that in the case of the $LaFe_{0.95}Pd_{0.05}O_3$ perovskite Pd is present on its surface and as Pd particles dissolved into it [18]. A comparison of perovskites obtained using different methods shows that Pd incorporates itself into the structure of $LaFeO_3$ when the perovskite is synthesized using the ultrasonic spray combustion and citric acid method [11] and the alkoxide method [6]. Mixed Pd^{2+}/Pd^0oxidation states indicating that Pd did not incorporate into the perovskite were observed

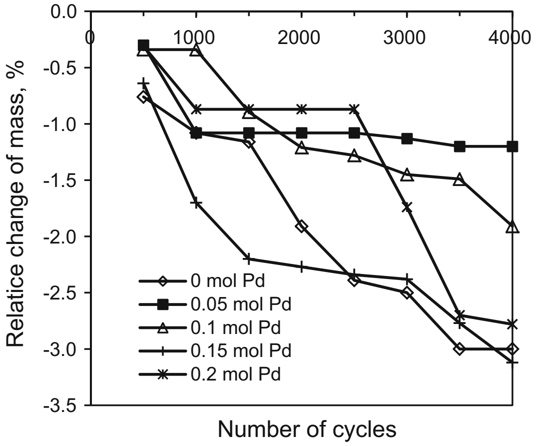

Fig. 7 Resistance of $La_{1-x}Pd_xMnO_3$ x = 0–0.2 catalysts to thermal shocks. Perovskite powders calcined at 750 °C for 6 h

when flame spray synthesis and solution combustion synthesis were used [11]. Regardless of the preparation method used, no Pd was introduced into the structure of the $LaMnO_3$ perovskite. Always PdO or PdO/Pd^0 supported on $LaMnO_3$ would be observed [11]. In the case of the $CaTiO_3$ perovskite, no solid solution with Pd forms [16, 19].

Since CO oxidation proceeds at high temperatures, not only the activity of the catalysts, but also good adhesion of the perovskites and the washcoat to the support is important. The latter was determined by testing the resistance of the catalysts to thermal shocks, i.e. to alternate heating to 1000 °C and cooling to room temperature. As a result of the rapid changes in temperature the washcoat and the active layer on the support may crack due to their different thermal expansion. The perovskites may peel off the support surface, whereby the activity of the catalyst deteriorates. The monolithic catalysts with $La_{1-x}Pd_xMnO_3$ show good resistance to alternate changes in temperature, which is indicative of good adhesion of the washcoat and the active layer to the support (Fig. 7). However, if palladium content in $La_{1-x}Pd_xMnO_3$ perovskite increases from 0.05 to 0.2 mol, there is a slight increase in the amount of active phase, which falls off the support during thermal shocks. After 4000 cycles of thermal shocks, the weight loss in the $La_{0.95}Pd_{0.05}MnO_3$ amounted to 1.2 % while that in the $La_{0.8}Pd_{0.2}MnO_3$ equalled 2.8 % (Fig. 7). When content of active phase in $La_{0.8}Pd_{0.2}MnO_3$-based catalyst is 3 g, the weight loss after 4000 cycles of thermal shocks is only 0.084 g.

4 Conclusions

Partial substitution of lanthanum or manganese by palladium in the $LaMnO_3$ perovskite-type oxides enhances the activity of perovskite-based metallic monolithic catalysts for CO oxidation.

The activity of the monolithic catalyst based on an $La_{1-x}Pd_xMnO_3$ perovskite increases with the quantity of palladium substituted for lanthanum (from 0.05 to 0.2 mol).

The $La_{0.85}Pd_{0.15}MnO_3$ catalyst with a perovskite obtained by the 4-h calcination of a mixture of lanthanum, manganese and palladium nitrates at 800 °C exhibits the highest activity for CO oxidation.

The activities of $LaMn_{1-x}Pd_xO_3$-based (x = 0.1 and 0.15) catalysts are influenced by the time and temperature of perovskite calcination and increase with the rise in calcination temperature from 650 to 850 °C.

Prepared under the same conditions, monolithic $La_{1-x}Pd_xMnO_3$-based catalysts display higher CO oxidation activities than do $LaMn_{1-x}Pd_xO_3$-based (x = 0.1 and 0.15) catalysts.

The activity of $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$-based catalysts is determined by the concentration of palladium on the catalyst surface. The size of the SSA of the perovskites has smaller influence on the activity of the catalysts.

$La_{1-x}Pd_xMnO_3$ (x = 0.05–0.2) perovskites exhibit good adhesion to the monolithic metal support.

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