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Effect of Pd additive on the activity of monolithic $LaMnO_3$-based catalysts for methane combustion

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Abstract

When the perovskites are calcined at 750 °C, the incorporation of Pd into $LaMnO_3$ enhances the activity of the catalyst in methane combustion at temperatures below 750 °C upon substitution of 0.1 mol La with Pd, and at temperatures below 600 °C when Pd is substituted for 0.1–0.15 mol Mn. Monolith catalysts based on $La_{1-x}Pd_xMnO_3$ ($x = 0.1, 0.15$) display a higher activity in methane combustion than do $LaMn_{1-x}Pd_xO_3$-based catalysts, which is due to the higher Pd/(Pd + Mn + La) ratio. The activities of the two perovskite types increase when calcination temperature is raised from 650 to 800 °C. With the increase in calcination temperature, an increase in the Pd content and a decrease in the La content is observed on the surfaces (X-ray photoelectron spectroscopy (XPS)). The rise in the temperature of perovskite calcination to 850 °C produces sintering which leads to the lowering in both the Pd content on the surfaces and the specific surface areas (SSAs) of the perovskites and, consequently, decreases catalytic activity.

Keywords: Methane combustion; Perovskites; Monolithic catalysts

1. Introduction

Perovskite catalysts (ABO_3) are well known for their activity and thermal resistance in CH_4 combustion. This activity can be enhanced by partial substitution of the metal in position A or B by other metal cations with similar ionic radii. In the case of the $LaMnO_3$ perovskite, Ag may replace La and Pd or Pt may replace Mn [1–6]. High activities were found to be those of the $La_{0.7}Ag_{0.3}Fe_{0.5}Co_{0.5}O_3$, $La_{0.7}Ag_{0.3}FeO_3$ [1], $La_{0.9}Ag_{0.1}MnO_3$ and $La_{0.7}Ag_{0.3}MnO_3$ [2,3].

Hydrocarbons have also been oxidized over catalysts where the perovskite surface was coated with Pd or the metal in position B of the perovskite was partly substituted with Pd [4,5]. The activity of Pd-doped perovskites is strongly influenced by the method of their preparation [4]. A three-way catalyst with Pd deposited onto the $LaFe_{0.8}Co_{0.2}O_3$ perovskite shows a noticeably higher activity and stability of performance than does a catalyst where some part of the Fe in the perovskite has been substituted with Pd ($LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$) [4]. Tanaka has reported that the Pd/$La_{0.9}Ce_{0.1}Co_{0.4}Fe_{0.6}O_3$ catalyst with Pd deposited onto the perovskite surface maintained a high three-way activity after ageing in a real engine exhaust gas [5]. There is also evidence that Pd- or Pt-based catalysts where the surfaces of the hexaaluminate materials ($LaAl_{11}O_{18}$ or $LaMnAl_{11}O_{19}$) were coated with Pd or Pt exhibit a high initial activity in CH_4 and CO oxidation [6]; the fresh Pt sample being less active than the Pd sample.

The aim of this study was to examine how a partial substitution of La or Mn with Pd in the $LaMnO_3$ perovskite influences the physicochemical properties (X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), BET) and activities of monolithic $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-y}Pd_yO_3$ catalysts for CH_4 combustion.

2. Methods of catalysts preparation and investigation

Monolithic catalysts were prepared on a support made of heat-resisting FeCr20%Al5% foils, with a honeycomb cross-section. The monolithic support was washcoated with Al_2O_3-TiO_2-La_2O_3 and calcined at 400 °C for 3 h. The $La_{1-x}Pd_xMnO_3$ ($x = 0$–0.2) and $LaMn_{1-y}Pd_yO_3$ ($y = 0.1, 0.15$) perovskites

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Table 1
Characterization of catalysts and perovskite powders

Composition of active phase	Calcination temperature (°C)	Calcination time (h)	Amount of active phase (%)	SSA of perovskites (m^2/g)	Mean pore diameter (nm)
$LaMnO_3$	750	6	11.5	8.6	8.5, 35[a]
$La_{0.95}Pd_{0.05}MnO_3$	750	6	12.1	10.6	25
$La_{0.95}Pd_{0.05}MnO_3$	800	4	14.2	7.6	10, 30[a]
$La_{0.9}Pd_{0.1}MnO_3$	750	6	12.0	9.4	15, 35[a]
$La_{0.85}Pd_{0.15}MnO_3$	650	8	13.0	12.3	16
$La_{0.85}Pd_{0.15}MnO_3$	750	6	12.4	8.8	9, 25[a]
$La_{0.85}Pd_{0.15}MnO_3$	800	4	12.3	6.1	20
$La_{0.85}Pd_{0.15}MnO_3$	850	4	12.9	3.5	60
$La_{0.8}Pd_{0.2}MnO_3$	750	6	12.1	9.4	15
$LaMn_{0.9}Pd_{0.1}O_3$	750	6	14.2	8.3	10
$LaMn_{0.9}Pd_{0.1}O_3$	800	4	13.4	6.8	12, 30[a]
$LaMn_{0.85}Pd_{0.15}O_3$	650	8	13.7	10.9	25–35
$LaMn_{0.85}Pd_{0.15}O_3$	750	6	13.1	9.0	12
$LaMn_{0.85}Pd_{0.15}O_3$	800	4	13.8	6.9	30
$LaMn_{0.85}Pd_{0.15}O_3$	850	4	13.9	4.7	23

[a] The pore distribution curve displays two maxima.

were obtained by mixing of $La(NO_3)_3{\cdot}6H_2O$, $Mn(NO_3)_3{\cdot}4H_2O$ and $Pd(NO_3)_2$, then dissolved in water, stirred, dried at 120 °C and calcined for 8 h at 650 °C, 6 h at 750 °C, 4 h at 800 °C and 4 h at 850 °C. The active phase was deposited by immersing the support in the slurry of the perovskite and citric acid. The catalysts were calcined at 500 °C for 3 h. The catalysts and the perovskite powders are characterized in Table 1.

Phase composition was examined by the X-ray diffraction method, using a Philips Materials research diffractometer. Measurements were carried out in the parallel beam optics. In the course of measurements, the active layer was illuminated at a constant angle ($\omega = 5°$), the scan being 2Θ. The surface composition of the catalysts was analyzed by X-ray photoelectron spectroscopy, using a SPECS UHV system equipped with a PHOIBOS 100 spectrometer and SpecLab software. BET specific surface areas (SSAs) were calculated from the nitrogen sorption isotherms measured by the static volumetric method at liquid nitrogen temperature, using an Autosorb-1-C/TCD instrument.

Catalytic activity was tested in the combustion of 1% methane in air, using a flow reactor placed in a heater (heating ramp 3 °C/min), total gas hourly space velocity (GHSV) being set to 15,500 h^{-1} (based on empty monolith support volume). Methane concentration was measured with a Sniffer analyzer (Bacharach).

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows examples of the XRD spectra obtained for the catalysts based on the $La_{0.85}Pd_{0.15}MnO_3$ perovskite calcined at 650–850 °C. The XRD spectra for the catalysts based on $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskites calcined at 650 °C have revealed the presence of the $LaMnO_{3.1}$ phase and PdO. There are also visible peaks ascribed to Fe-Cr coming from the heat-resisting foil of which the support has been made. The remarkable background bump in the spectra of these catalysts substantiates the presence of large amounts of amorphous phase. Upon calcination of the $La_{1-x}Pd_xMnO_3$ and $LaMn_{1-x}Pd_xO_3$ ($x = 0.1$, 0.15) perovskites at 750 °C, the XRD displayed a metallic Pd peak in addition to the peaks ascribed to the $LaMnO_{3.1}$ phase and Fe-Cr. The spectra of the monolithic

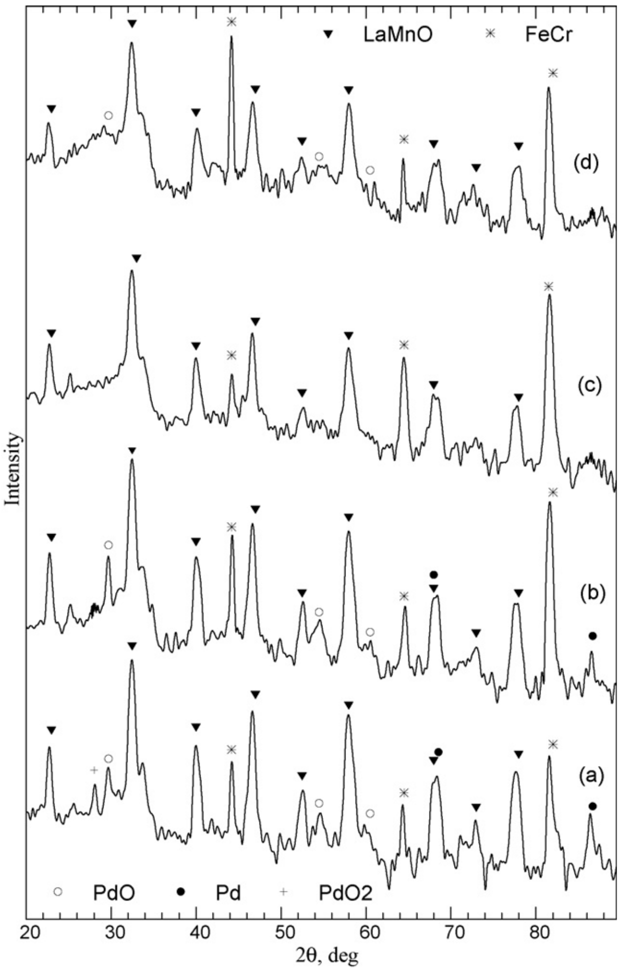

Fig. 1. XRD patterns of fresh monolithic $La_{0.85}Pd_{0.15}MnO_3$ catalysts. Calcination temperature of perovskites: (a) 850 °C; (b) 800 °C; (c) 750 °C; (d) 650 °C.

catalysts based on the perovskites mentioned that were calcined at 800 or 850 °C have revealed the presence of the $LaMnO_{3.1}$, Pd, PdO and PdO_2 phases, as well as peaks ascribed to Fe-Cr.

In both $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ catalysts calcined at 750 °C, thermal reduction of Pd^{2+} induces the occurrence of metallic Pd, which segregates to the surfaces of the perovskites. While the perovskites that were calcined at 800 or 850 °C are being cooled in air, metallic Pd on their surfaces undergoes oxidation to PdO and PdO_2 (XRD). A similar effect has been reported for mixed Pd-perovskite automotive catalysts [7–11].

3.2. XPS measurements

Measured by the XPS method, the surface composition of the perovskite examined was found to differ from the volume composition. The values of the Pd/La and Mn/La ratios that are lower than the stoichiometric ones point to the enrichment of the perovskite surfaces with the lanthanum segregating to the surface (Table 2). The quantity of palladium on the surfaces of the perovskites expressed as the Pd/(Pd + Mn + La) ratio increases with the rise in calcination temperature from 650 to 800 °C, which is attributable to the segregation of Pd to the surface. In the perovskites calcined at 850 °C the Pd/(Pd + Mn + La) ratio decreases, which is associated with the agglomeration of palladium on the surface (the XPS method underrates the measured concentration values for crystallites larger in size than several nanometers).

The XPS spectra of the palladium substituted into the structure of the $LaMnO_3$ perovskites are diverse. The differences in the spectra, accounted for by the Pd content and the temperature of perovskite calcination, begin to manifest in the half-intensity widths (FWHM) of the recorded Pd 3d peaks, which vary from 1.54 to 3.34 eV. Lower FWHM values (<1.9 eV) are observed with $La_{1-x}Pd_xMnO_3$, and substantially higher (>2.2 eV) with $LaMn_{1-x}Pd_xO_3$ perovskites. The narrow and pointed Pd $3d_{5/2}$ peaks for $La_{1-x}Pd_xMnO_3$ ($x = 0.1, 0.15$) with a maximum at approx. 336.5 eV can be ascribed to PdO, while the wide shapes of the peaks in $LaMn_{1-x}Pd_xO_3$ imply that Pd is present as Pd^0, Pd^{2+}, $Pd^{3+}$and Pd^{4+} [12].

Also in the two groups of the perovskites heated at 500–600 °C (in a UHV XPS chamber with hydrogen as a main component of residual gases) Pd was found to follow a different behavioral pattern. As for $La_{1-x}Pd_xMnO_3$, a practically complete reduction of $Pd^{2+} \rightarrow Pd^0$ was observed with a shift of BE from 336.4 to 334.4 eV (Fig. 2). In the case of $LaMn_{1-x}Pd_xO_3$, the Pd 3d spectra displayed a broad shape of the peak and a considerable quantity of Pd^{2+}. The shape of the peak does not permit the presence of Pd^{3+} and Pd^{4+} to be excluded [7]. However, the deconvolution of the peaks (which is indispensable) requires further studies.

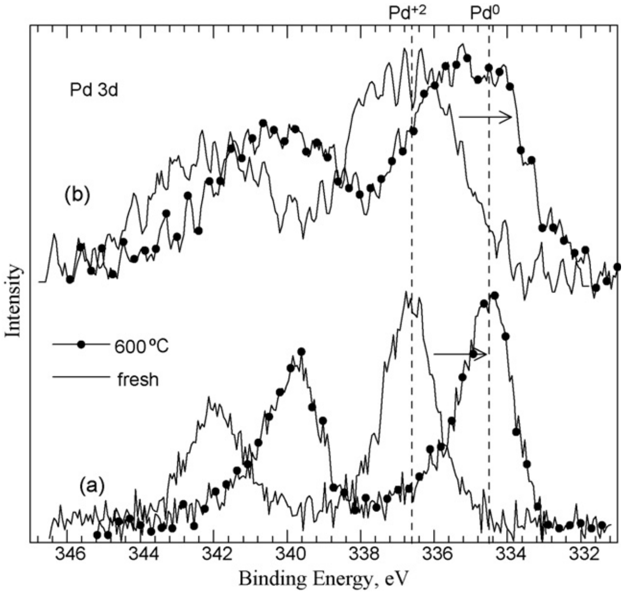

Fig. 2. XPS spectra of Pd 3d for $La_{0.85}Pd_{0.15}MnO_3$ (a) and $LaMn_{0.9}Pd_{0.1}O_3$ (b) catalysts.

The maximum of the peak of the Mn $2p_{3/2}$ spectrum for the $La_{1-x}Pd_xMnO_3$ perovskites calcined at 750 °C amounts to 641.6 eV; their FWHMs differ only slightly, falling in the range of 3.05–3.1 eV. For $LaMn_{1-x}Pd_xO_3$, the FWHMs are wider, amounting to 3.85 eV. Apart from the maximum at 641.6 eV (characteristic for Mn^{3+}), there is also a component of a lower BE at 640.5 eV, which has been ascribed to Mn^{2+} [13,14]. At about 500 °C, in vacuo, the manganese that was present on the catalyst surface underwent partial reduction, which manifests in the maximum of the Mn $2p_{3/2}$ peak shifted towards 641.1 eV. With the perovskites calcined at 800 °C, the Mn 2p spectra are identical for the two perovskite types. The maxima of the peaks occur in position Mn^{3+}, at 641.52 eV, and their FWHMs amount

Table 2
Surface composition of perovskite catalysts compared to the stoichiometric one

Catalyst	Pd/La	Pd/Mn	Mn/La	Pd/(Pd + Mn + La)
$LaMn_{0.85}Pd_{0.15}O_3$ (650 °C)	0.01 (0.15)[a]	0.09 (0.18)	0.12 (0.85)	0.009 (0.075)
$LaMn_{0.85}Pd_{0.15}O_3$ (750 °C)	0.03 (0.15)	0.10 (0.18)	0.27 (0.85)	0.021 (0.075)
$LaMn_{0.85}Pd_{0.15}O_3$ (800 °C)	0.08 (0.15)	0.29 (0.18)	0.33 (0.85)	0.056 (0.075)
$LaMn_{0.85}Pd_{0.15}O_3$ (850 °C)	0.07 (0.15)	0.24 (0.18)	0.27 (0.85)	0.048 (0.075)
$La_{0.85}Pd_{0.15}MnO_3$ (650 °C)	0.02 (0.18)	0.09 (0.15)	0.22 (1.18)	0.016 (0.075)
$La_{0.85}Pd_{0.15}MnO_3$ (750 °C)	0.06 (0.18)	0.09 (0.15)	0.61 (1.18)	0.034 (0.075)
$La_{0.85}Pd_{0.15}MnO_3$ (800 °C)	0.08 (0.18)	0.12 (0.15)	0.69 (1.18)	0.046 (0.075)
$La_{0.85}Pd_{0.15}MnO_3$ (850 °C)	0.06 (0.18)	0.081 (0.15)	0.76 (1.18)	0.034 (0.075)
$La_{0.9}Pd_{0.1}MnO_3$ (750 °C)	0.06 (0.11)	0.09 (0.10)	0.62 (1.11)	0.034 (0.05)
$LaMn_{0.9}Pd_{0.1}O_3$ (750 °C)	0.03 (0.10)	0.16 (0.11)	0.20 (0.90)	0.026 (0.05)

[a] Stoichiometric atomic ratios are presented in parentheses.

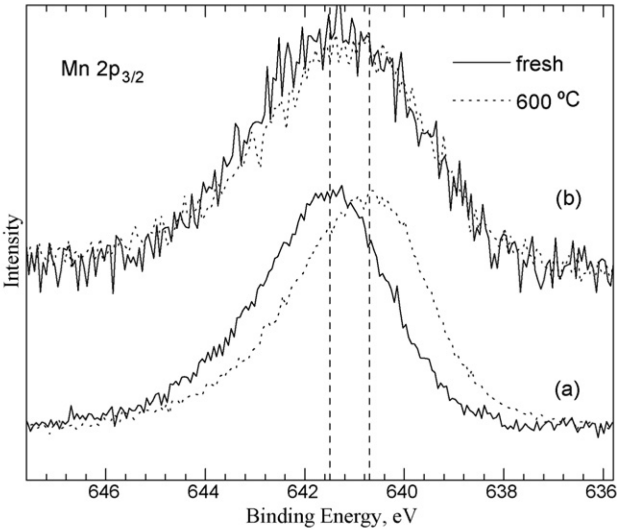

Fig. 3. XPS spectra of Mn $2p_{3/2}$ for $LaMn_{0.85}Pd_{0.15}O_3$ catalysts calcined at 800 °C (a) and 750 °C (b).

to 3.05 eV. At 500 °C, manganese undergoes reduction more readily; the maximum of the Mn $2p_{3/2}$ peak shifts to 640.7 eV, and the narrow shape of the peak is preserved (Fig. 3).

3.3. Catalyst activity testing

The substitution of some part of lanthanum with palladium in the $LaMnO_3$ perovskite calcined at 750 °C enhances catalyst activity in methane combustion (Fig. 4a). A distinct rise in activity is observed with the $La_{0.9}Pd_{0.1}MnO_3$-based catalyst. Over the $La_{0.85}Pd_{0.15}MnO_3$ and $La_{0.8}Pd_{0.2}MnO_3$ catalysts, at temperatures lower than 650 °C, methane conversion was substantially higher than over the $LaMnO_3$ catalyst. At higher temperatures the activities of the two catalysts approach the activity of the $LaMnO_3$ catalyst.

Activity tests were also conducted with monolithic $LaMn_{1-y}Pd_yO_3$ ($y = 0.1$, 0.15) catalysts (perovskites were calcined at 750 °C). Their activity is slightly lower than that of the catalysts where La was substituted with Pd (Fig. 4b). This is attributable to the smaller quantity of Pd on the surfaces of catalysts. Thus, with $LaMn_{0.85}Pd_{0.15}O_3$, the Pd/(Pd + La + Mn) ratio is 0.021 while with $La_{0.85}Pd_{0.15}MnO_3$ it is 0.034 (XPS). If we prepare a perovskite which has a stoichiometric composition of $La_{0.85}Pd_{0.15}MnO_3$ type, excessive palladium will occur in the form of PdO and PdO_2. The higher content of very active palladium in the $La_{1-x}Pd_xMnO_3$ perovskites (as compared to $LaMn_{1-x}Pd_xO_3$) accounts for their enhanced activity in CH_4 combustion. The activities of the catalysts based on $LaMn_{1-x}Pd_xO_3$ ($x = 0.1$, 0.15) perovskites are higher than the activity of the $LaMnO_3$-based catalyst only at temperatures below 600 °C.

The activities of the $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ catalysts based on perovskites that were calcined at 650 °C are low (Fig. 5), which is attributable to the low palladium content on the catalyst surface (XPS). XRD analyses of the catalysts have revealed the presence of considerable amounts of amorphous phase. Despite the lower BET surfaces of the perovskites calcined at 800 °C as compared to the perovskites calcined at 650 or 750 °C, the activity of the $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ catalysts (all calcined at 800 °C) are slightly higher than the activities of the catalysts based on the same perovskites that were calcined at 650 or 750 °C (Fig. 5). XPS examinations have shown that the rise in the calcination temperature for the $LaMn_{0.85}Pd_{0.15}O_3$ perovskite from 650 to 800 °C increases the proportion of the surface Pd with respect to (Pd + Mn + La) from 0.9 to 5.6 at.% and, at the same time, reduces the proportion of La from 89 to 71 at.%, thus enhancing the activity of the catalyst. A further rise in the calcination temperature for the perovskite from 800 to 850 °C decreases the Pd content on the surface to 4.8 at.% and notably

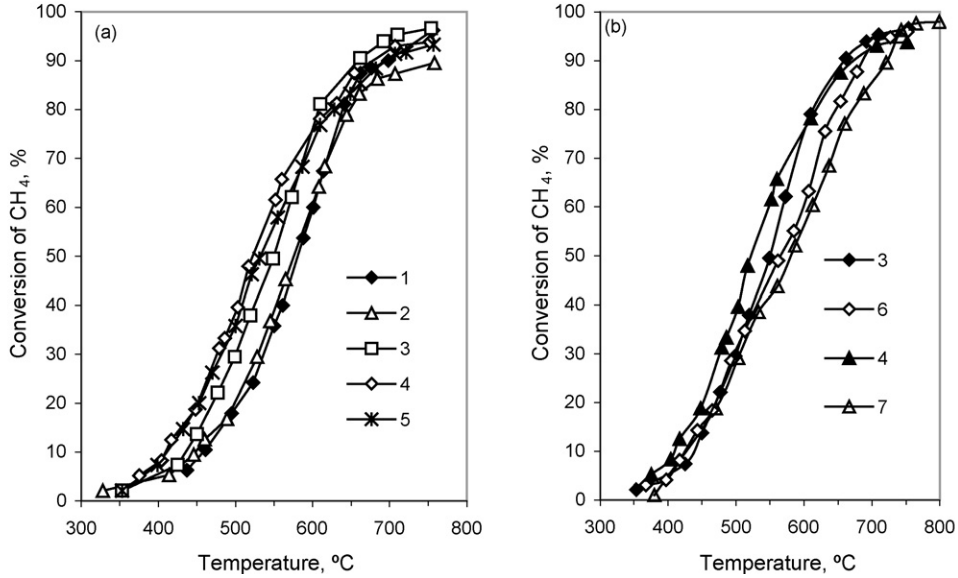

Fig. 4. Methane conversion as a function of temperature for $La_{1-x}Pd_xMnO_3$ (a) and $LaMn_{1-y}Pd_yO_3$ (b) catalysts. (1) $LaMnO_3$; (2) $La_{0.95}Pd_{0.05}MnO_3$; (3) $La_{0.9}Pd_{0.1}MnO_3$; (4) $La_{0.85}Pd_{0.15}MnO_3$; (5) $La_{0.8}Pd_{0.2}MnO_3$; (6) $LaMn_{0.9}Pd_{0.1}O_3$; (7) $LaMn_{0.85}Pd_{0.15}O_3$. Perovskite powders calcined at 750 °C for 6 h.

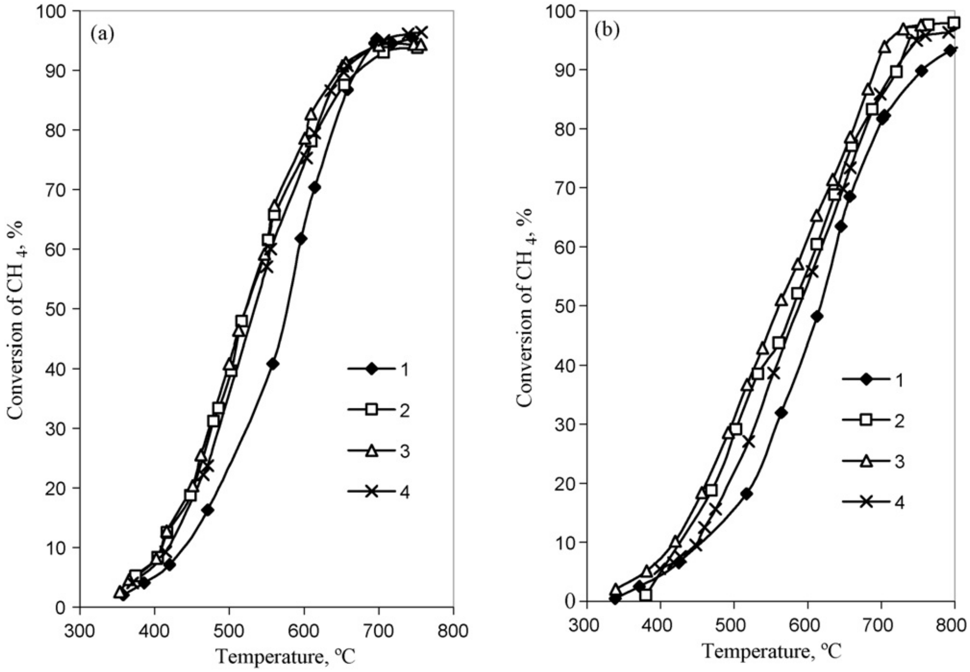

Fig. 5. Comparison of methane combustion as a function of calcination temperature of perovskites for $La_{1-x}Pd_xMnO_3$ (a) and $LaMn_{1-y}Pd_yO_3$ (b) catalysts. Calcination temperature: (1) 650 °C; (2) 700 °C; (3) 800 °C; (4) 850 °C.

reduces the SSA (4.7 m^2/g), thus accounting for the decrease in the activity of the $LaMn_{0.85}Pd_{0.15}O_3$ catalyst. A similar pattern has been observed in the case of the $La_{0.85}Pd_{0.15}MnO_3$ perovskite catalyst (Tables 1 and 2). In the presence of the $La_{0.85}Pd_{0.15}MnO_3$ catalyst (with perovskite calcined at 800 °C), the temperatures T_{10}, T_{50} and T_{90} amount to 410, 520 and 645 °C, respectively. When the calcination temperature for the perovskite was increased to 850 °C, the values of T_{10}, T_{50} and T_{90} rose to 418, 532 and 655 °C, respectively. The rise in these temperatures was due to the perovskite sintering which produced a decrease in the SSA from 6.1 m^2/g (at 800 °C) to 3.5 m^2/g (at 850 °C) and in the Pd/(Pd + Mn + La) ratio from 0.046 to 0.034. Cimino et al. [9] has reported that in the combustion of 0.4% CH_4 with a mixture containing 10% O_2, in the presence of a 2.5 wt.% Pd-$LaMnO_3$ catalyst (calcined at 800°C), T_{10}, T_{50} and T_{90} approached 420, 500 and 610 °C, respectively. Upon heating at 900 °C for 1 h under reaction atmosphere, the catalyst became activated and the values of T_{10}, T_{50} and T_{90} decreased to 280, 340, 390 °C, respectively. In our study, catalysts based on $La_{0.85}Pd_{0.15}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskites calcined at 800 °C for 4 h displayed the highest activity in CH_4 combustion. For both the catalysts the increase in calcination temperature to 850 °C gave rise to the sintering of the perovskites, which reduced considerably not only their SSAs but also their Pd/(Pd + Mn + La) ratios on the surfaces, thus decreasing catalyst activity (Fig. 5).

4. Conclusions

The incorporation of Pd into the $LaMnO_3$ perovskite enhances the activity of the catalyst in CH_4 combustion. As compared to the $LaMnO_3$-based catalyst, monolithic catalysts based on $La_{0.9}Pd_{0.1}MnO_3$, $La_{1-x}Pd_xMnO_3$ ($x = 0.15$–0.2) and $LaMn_{1-y}Pd_yO_3$ ($y = 0.1, 0.15$) perovskites calcined at 750 °C display a higher activity in methane combustion at temperatures below 750, 650 and 600 °C, respectively. The monolithic $La_{1-x}Pd_xMnO_3$ ($x = 0.1, 0.15$)-based catalysts show a higher activity than do those based on $LaMn_{1-x}Pd_xO_3$ perovskites. On the surface of $La_{1-x}Pd_xMnO_3$ palladium occurs mainly in the form of PdO which is readier to undergo a complete cyclic reduction and oxidation.

When calcined at 800 °C for 4 h, despite their lower BET surfaces, $La_{0.85}Pd_{0.15}MnO_3$, $La_{0.95}Pd_{0.05}MnO_3$ and $LaMn_{0.85}Pd_{0.15}O_3$ perovskites show slightly higher activities than when calcined at 750 °C for 6 h. With a higher calcination temperature, an increase in the Pd content and a decrease in the La content were observed on the perovskite surfaces. The rise in the temperature of perovskite calcination to 850 °C decreases slightly the activity of the catalysts. This is due to the perovskite sintering (decrease in the SSA) and to the reduction in the Pd content on the perovskite surfaces (XPS).

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