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Effect of Pd or Ag additive on the activity and stability of monolithic $LaCoO_3$ perovskites for catalytic combustion of methane

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Abstract

The $LaCoO_3$ perovskite-type catalysts in this study were monoliths resting on supports made of heat-resisting foil and washcoated with Al_2O_3. The $La_{0.9}Ag_{0.1}CoO_3$ or $La_{0.92}Pd_{0.08}CoO_3$ perovskite was used as the active phase. Partial substitution of lanthanum in the $LaCoO_3$ perovskite with palladium or silver enhances the activity of the monolithic catalysts in the combustion of methane. XPS and XRD analyses show that during approximately 500 h on stream (at 750 and 704 °C, respectively) the surface composition of the $La_{0.9}Ag_{0.1}CoO_3$ catalyst and that of the $La_{0.92}Pd_{0.08}CoO_3$ catalyst undergoes considerable changes. In both the catalysts, cobalt and aluminum oxide segregate to the surface while the amount of carbonate groups decreases. In the $La_{0.92}Pd_{0.08}CoO_3$ catalyst, the amount of palladium and the average oxidation state of Pd on the surface increase. On the surface of the $La_{0.9}Ag_{0.1}CoO_3$ catalyst, the amount of silver decreases, and Ag in the metallic state oxidizes to Ag^+, which probably becomes built-in the perovskite structure. In spite of these changes, the catalysts display a high activity and a good stability during above 500 h of methane combustion.

Keywords: Methane combustion; Perovskites; Monolithic catalyst

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1. Introduction

Catalytic methane combustion has become a convenient method of heat and energy acquisition, as well as gas emission control. In this process, perovskite-type oxides, ABO_3 (where A is usually a rare earth cation and B a transition metal cation), have been found to display good catalytic properties and thermally stability [1,2]. The catalytic properties of the perovskite depend primarily on the type of cation B, the contribution of the metal in position A being less important [1]. The highest catalytic activity is that of the perovskites with lanthanum as metal A ($LaBO_3$ perovskites), and Co, Mn, Fe, Cr or Ni as metal B [3–9], although Nd ($NdCoO_3$) has also been used as metal A [10]. A large active group for methane combustion includes $AFeO_3$ perovskites (with metal A being La, Nd or Sm) [11]. Reports are also available on the application of perovskites in which the metal in position A and/or B has been partly substituted with another metal, thus establishing a large group of active oxides described by the general formula $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$, where δ stands for excess oxygen resulting from the non-stoichiometry of these species [7–9]. The type and the amount of the metal to be substituted for the one in position A may stabilize an unusual of oxidation state of the cation in position B and/or produce oxygen vacancies or structural defects [2,7,9]. Structural defects change the physicochemical properties of the perovskite, thus favouring the transport of ion within the oxide framework, and this brings about some interesting differences in the catalytic properties [2]. Partial substitution of lanthanum with divalent ions, e.g. Sr^{2+}, increases the average oxidation state of the cation in position B. When Co or Fe are in position B, this generates anionic vacancies. Owing to the relative ease for the redox process to occur between B^{4+} and B^{3+}, larger quantities of oxygen become available at low temperature, thus enhancing the overall activity of the system [1]. Catalytic activity can be raised by a partial substitution of lanthanum in $LaCoO_3$ and $LaMnO_3$ with Ce, Eu or Sr [2,8,12,13], but it is also advantageous to substitute the lanthanum incorporated in the $LaFeO_3$ perovskite with strontium or cerium ($La_{1-x}A_xFeO_3$) [14,15]. Of the catalysts belonging to this group the most active are $La_{0.8}Sr_{0.2}FeO_3$

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and $La_{0.7}Ce_{0.3}FeO_3$. The $LaFeO_3$ perovskite displays a high activity even if some part of the lanthanum ingredient is substituted with cerium and strontium ($La_{1-x-y}Sr_xCe_yFeO_3$) [14]. Attempts have also been reported to substitute partly the transition metal at site B with another trivalent cation. Examining the $LaFe_{1-x}M_xO_3$ (M = Al, Mn, Co) [1], a synergistic effect due to the presence of two types of cations B has been detected, which improved their average oxidation state and enhanced their capability of methane combustion. The substitution of the iron or manganese incorporated in the $LaFeO_3$ and $LaMnO_3$ perovskites with copper or copper and iron, respectively, does not raise catalytic activity [9]. When magnesium is substituted for manganese in the $LaMnO_3$ perovskite ($LaMn_{1-x}Mg_xO_3$), the effect is positive with a low amount of magnesium ($x \leq 0.2$) [10]. A high activity in the combustion of hydrocarbons is characteristic of catalysts where the metal in position A has been substituted with silver. Such is, for example, the catalyst $La_{0.7}Ag_{0.3}Fe_{0.5}Co_{0.5}O_3$ [16] or the catalyst $La_{0.7}Ag_{0.3}MnO_3$ which displays a higher activity in methane combustion than does the $La_{0.7}Sr_{0.3}MnO_3$ catalyst [17]. In perovskites of $La_{1-x}Ag_xMnO_3$ type, a homogeneous structure in the absence of inactive metallic silver is obtained with $x \leq 0.2$ [18]. Attempts have also been made to substitute the metal in position B by palladium or to spread palladium onto the perovskite surface. The $Pd/LaFe_{0.8}Co_{0.2}O_3$ catalyst shows a higher activity in the combustion of hydrocarbons as compared to the $LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$ catalyst [19].

For methane combustion, use is made of monolithic honeycomb catalysts, prepared by extruding plastic pastes composed of perovskite powders, with the addition of binders, acid peptizers and some surfactants [20]. The perovskite may also be spread onto an appropriate monolithic cordierite support, often washcoated, e.g. with γ-Al_2O_3. Such perovskite is easy to form and displays a low thermal expansion. Compared to powders of the same chemical composition, the deactivation of a monolithic catalyst is much lower [4,6]. However, a high calcination temperature may reduce the specific surface area of the catalyst and/or sinter the metal oxides with the support material.

The literature contains references to perovskites with silver-substituted metal in position A or with palladium incorporated into the perovskite, which showed a high catalytic activity in the combustion of hydrocarbons. In our study, we tested the activity of such perovskites in the combustion of methane, which is very difficult to oxidize. The study reported on in this paper was carried out with two monolithic perovskite catalysts resting on supports made of heat-resisting foil. The active phase was an $La_{1-x}M_xCoO_3$ (M = Ag, Pd) perovskite. The variations in the composition of the catalysts, with $La_{0.9}Ag_{0.1}CoO_3$ or $La_{0.92}Pd_{0.08}CoO_3$ as an active phase after 500 h of methane combustion were determined by the XRD and XPS methods. The catalysts were also investigated for activity and stability of performance.

2. Methods of catalysts preparation and investigation

The perovskite catalysts rested on monolithic supports made of 00H20J5-type heat-resisting foil (Baildon Steelworks, Poland). The support (cylindrical in shape, 70 mm high and 26 mm in diameter, with a honeycomb cross-section and triangular canals) was cladded with an Al_2O_3 washcoat by the sol–gel method. The active phase consisted of perovskite-type oxides, $LaCoO_3$, $La_{0.9}Ag_{0.1}CoO_3$ or $La_{0.92}Pd_{0.08}CoO_3$, obtained by calcination of appropriate amounts of $La(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot H_2O$, and $AgNO_3$ or $Pd(NO_3)_2$ at 750 °C for 6 h. The active layer was deposited onto the washcoated support by immersion in the slurry obtained from perovskite powder and citric acid. The catalysts were calcined in air at 500 °C for 3 h. The amount of the deposited active layer approached 12 wt.%.

Phase composition was examined by the X-ray powder diffraction (XRD) 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 ($\omega = 5^\circ$), the scan being 2Θ.

Surface characterization and depth profile composition examinations were carried out with fresh catalysts and after 500 h of performance by X-ray photoelectron spectroscopy (XPS), using a SPECS UHV system equipped with a PHOIBOS 100 spectrometer and Speclab software. The X-ray source was generated with an Mg anode operating at 100 W (survey scan) and 200–300 W (high resolution spectra). The analyzer mode was set at constant pass energy (30 eV, survey scan; 5 eV, narrow scan). Sample charging was compensated, using an electron flood at 0.5 mA current and 0.1 eV energy. The detection angle was normal to the surface.

The BET surfaces of the perovskites was measured by nitrogen adsorption at 77 K, assuming 0.162 nm^2 as the area of the adsorbate molecule. Samples were dehydrated under vacuum at 300 °C for 3 h, before surface area estimations.

Methane combustion tests were carried out in a laboratory throughflow reactor placed in an electric oven. Use was made of a gas mixture containing 1 vol.% of methane in air, gas flow velocity being set to 5800 h^{-1}. The catalyst in the reactor was heated at a constant rate of 3°/min until the given temperature was achieved, and thereafter stabilized for 30 min; then the concentrations of methane, carbon oxide and nitrogen oxides in the gas effluent were determined. The reaction temperature was increased, and measurements of CH_4, CO and NO_x concentrations were performed until the temperature reached a level at which methane conversion approached 96–97%.

The stability of methane combustion over the two catalysts $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ was investigated approximately during 500 h. The combustion of 1 vol.% of methane in air in the presence of these catalysts was carried out at 750 and 704 °C, respectively, at a space velocity of 4500 h^{-1}.

Methane concentration was measured with a Sniffer analyzer (Bacharach). Monoxor II and Nonoxor II analyzers (Bacharach) were used to measure the concentrations of CO and NO_x, respectively.

3. Results and discussion

3.1. X-ray diffraction

The XRD spectra of the $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ catalyst samples before (fresh catalyst) and after 500 h of methane combustion at 750 and 704 °C, respectively, are presented in Fig. 1. As shown by the spectra of the active phase, calcination at 750 °C for 6 h does not lead to a complete transition of lanthanum, cobalt and silver or palladium nitrates from the mixture to the perovskite $LaCoO_3$, because $La_4Co_3O_{10}$ and $AgCoO_2$ or $La_2Pd_2O_5$ are still present besides the active phase. In the XRD spectra of the catalysts after 500 h on stream the $LaCoO_3$ perovskite alone is visible. This suggests that the calcination time for the mixture of nitrates during perovskite synthesis at 750 °C should be extended.

3.2. XPS measurements

XPS examinations of the $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ catalysts before and after the run revealed some changes in the composition of their surfaces, as it can be seen in Table 1. Oxygen was found to occur in noticeable excess on the catalyst surface both before and after the run. Before the run, the surfaces of the two catalysts exhibited far less cobalt than it could be inferred from the stoichiometry. The Co/La ratio was 0.0 and 0.02 for $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$, respectively. After the run, a considerable segregation of cobalt to the surface was observed, and the Co/La ratio increased to 0.184 and 0.29, respectively.

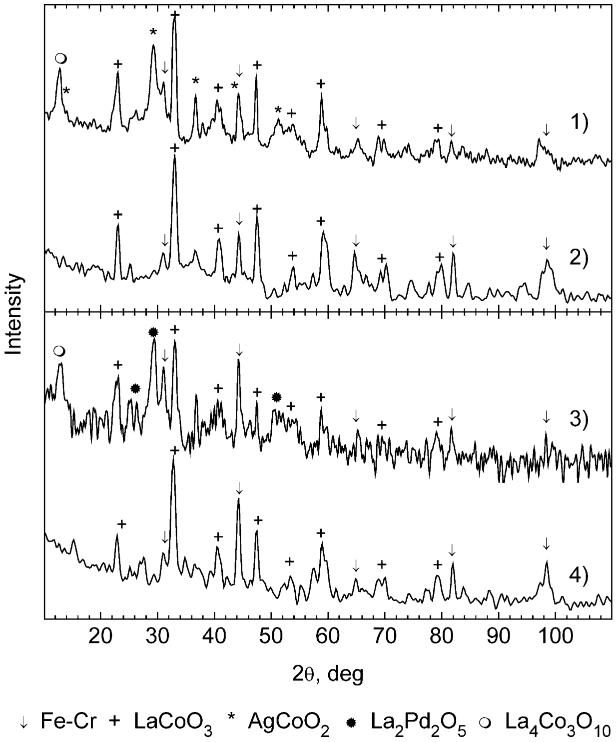

Fig. 1. XRD spectra of active phases $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ after calcination at 750 °C for 6 h. XRD patterns of: fresh $La_{0.9}Ag_{0.1}CoO_3$ (1), after 500 h on stream (2), fresh $La_{0.92}Pd_{0.08}CoO_3$ (3), after 500 h on stream (4).

Table 1
Surface composition of the perovskite catalysts (before and after 500 h on stream) determined by XPS

Composition of active phase	Atom concentration (at. %)						
	La	Co	Ag	Pd	O	C	Al
$La_{0.9}Ag_{0.1}CoO_3$							
Fresh state	10.22	0	9.03	–	69.51	11.25	0
After 500 h on stream	6.93	1.28	0.8	–	64.45	3.99	22.55
$La_{0.92}Pd_{0.08}CoO_3$							
Fresh state	14.10	0.33	–	0.16	71.02	14.39	0.0
After 500 h on stream	6.75	1.95	–	0.22	61.88	3.02	26.18

The XPS spectra of lanthanum for both catalysts are difficult to interpret because of the presence of satellite peaks. For lanthanum, the closed-shell La^{3+} ion shows its La $3d_{5/2}$ and La $3d_{3/2}$ peaks split by approximately 4 eV into two components, which has been assigned to the transfer of an oxygen-centered electron to the empty 4f shell accompanying the ionization process. These energy loss peaks appearing on the high energy side of the $3d_{5/2}$ and $3d_{3/2}$ peaks in Fig. 2 are referred to as satellite peaks. The satellite peak intensity in the La 3d doublet varies with temperature [21]. The La $3d_{5/2}$ feature for the fresh $La_{0.9}Ag_{0.1}CoO_3$ catalyst is recorded at 835 and 838.5 eV. These values are the same as the ones for pure La_2O_3 (Fig. 2c and d). The La 3d peaks for the catalyst after 500 h on stream (Fig. 2b) are wider (which suggests an increase in the extent of structural disorder), and they are shifted towards lower energies by about 0.5 eV. Like the XRD results, the XPS spectra confirm the formation of the perovskite structure. All lanthanum ions occur in the form of La^{3+}.

In the fresh $La_{0.92}Pd_{0.08}CoO_3$ catalyst the proportion of palladium to lanthanum on the surface was one-eighth that assumed stoichiometrically (Pd/La = 0.01). After 500 h on stream (Table 1), the catalyst surface displayed an over three-fold Pd-enrichment (Pd/La = 0.033). Fig. 3 shows the XPS spectra of Pd 3d for this catalyst. In the fresh catalysts, the BE of Pd $3d_{3/2}$ amounting to 337.2 eV corresponds with that of PdO (Fig. 3a); after the run (Fig. 3b), it has shifted towards higher energies by 0.8 eV. This implies an increase in the average oxidation state of palladium, which might have reduced the activity of the catalyst after 500 h on stream. Pd was not found to occur in metallic form.

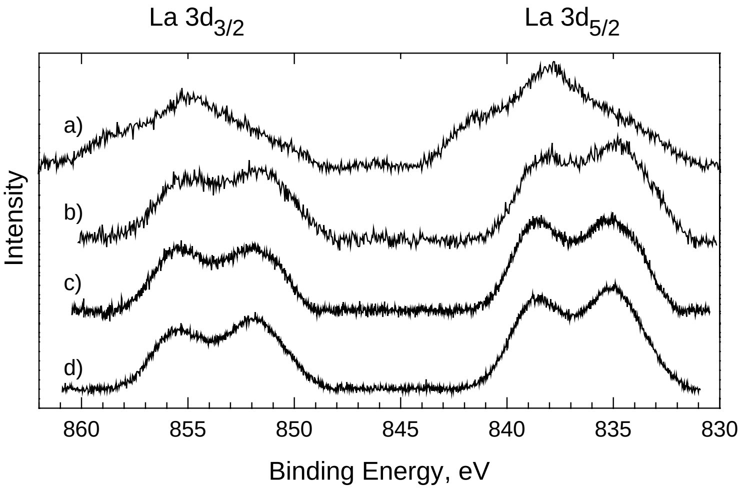

Fig. 2. XPS spectra of La 3d in $LaCoO_3$ perovskite (a), in $La_{0.9}Ag_{0.1}CoO_3$ catalyst after the run (b), in fresh $La_{0.9}Ag_{0.1}CoO_3$ catalyst (c), in La_2O_3 (d).

The position of the Ag 3d line in the XPS spectrum of the fresh $La_{0.9}Ag_{0.1}CoO_3$ catalyst (Fig. 4c) at 368.25 and 374.25 indicates that silver occurs in the form of Ag^0. The proportion of silver to lanthanum measured in this catalyst is considerably higher than the stoichiometric one ($Ag/La = 0.89$). Also SEM images reveal the presence of silver crystallites on the catalyst surface, although silver is invisible in the XRD spectra (Fig. 1). This apparent discrepancy can be explained after examinations of the depth profiles obtained by alternating Ar^+ etching of the sample surface and XPS analysis. It has been found that as soon as several nanometers of the surface layer have been etched, silver concentration decreases rapidly and the Ag/La ratio amounts to 0.07 to stabilize at the level of 0.04–0.05 after further etching. This is in quite a good agreement with the expected values for the entire sample bulk. However, it was found that in the sample bulk (after etching) the BE for Ag $3d_{5/2}$ is shifted towards lower energies and equals 367.45 eV. This energy was assigned to $AgCoO_3$, as the presence of this compound was revealed by XRD analysis. According to Gulari et al. [22], the BE for Ag $3d_{5/2}$ in $AgCoO_2$ is 367.6 eV. The difference of 0.15 eV may be attributed to the unavoidable surface reduction by Ar^+ etching. Measurements performed after the run showed that the amount of silver on the catalyst surface decreased, and the Ag/La ratio equaled 0.115. The Ag/La ratio in depth profiling amounted to 0.05, so its value was similar to that of a fresh catalyst. The BE for Ag 3d, which was 367.9 and 373.9 eV, respectively (Fig. 3d), did not very much differ from the BE obtained for Ag_2O (368 and 374 eV, respectively; Fig. 3b). As the XRD examinations revealed no presence of Ag_2O or Ag_2CO_3, there is great probability that the silver in the form of Ag^+ has been built-in into the $LaCoO_3$ perovskite lattice.

The C 1s core-level showed mainly two components in all spectra. According to Fierro [23], one of these, at 284.8 eV, comes from hydrocarbon contamination; the other one, around 288.7 eV, is typical of carbonate species. Lanthanum carbonates and oxycarbonates are very stable at temperature up to 1000 °C [24], and their high surface concentration reduces catalytic activity [25]. After the run,

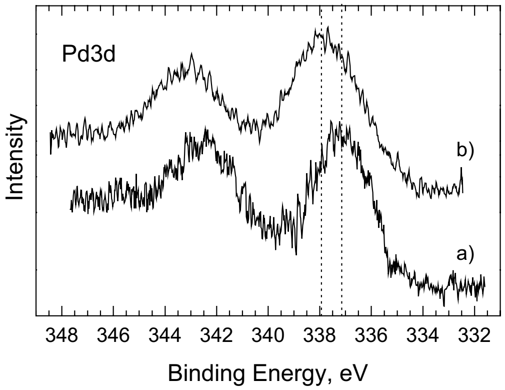

Fig. 3. XPS spectra of Pd 3d in fresh $La_{0.92}Pd_{0.08}CoO_3$ catalyst (a), in the same catalyst after 500 h on stream (b).

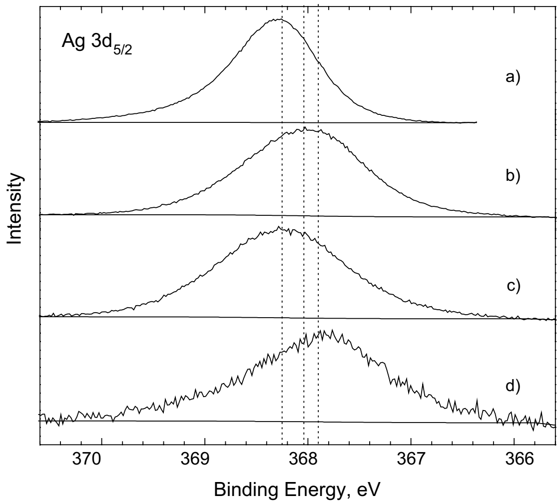

Fig. 4. XPS spectra of Ag 3d in Ag (a), Ag_2O (b), fresh $La_{0.9}Ag_{0.1}CoO_3$ catalyst (c), in the same catalyst after 500 h on stream (d).

a noticeable decrease in the amount of carbonate groups was detected in the two perovskite catalysts studied. The $C_{carbonates}$/La ratio in each of them approached 1 and 0.5 before and after the run, respectively.

No presence of washcoat Al_2O_3 was detected on the surfaces of the fresh $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ catalysts. However, after 500 h on stream a considerable portion of Al_2O_3 segregated from the washcoat to the catalyst surface, so that the Al_2O_3 content became over three times as high as the lanthanum content (Table 1).

3.3. Catalyst activity testing

The test reaction of methane combustion was carried out over monolithic catalysts with $LaCoO_3$, $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.9}Pd_{0.08}CoO_3$ as the active phase (calcined for 6 h at 750 °C) and over an $LaCoO_3$ catalyst (calcined for 20 h at 750 °C), according to the reaction temperature applied. The values of T_{10}, T_{50} and T_{90} (temperatures at which methane conversion reaches 10, 50 and 90%, respectively) for fresh catalysts and after 500 h on stream, as well as those of the BET surfaces for the active phases, are gathered in Table 2.

The extension of the calcinations time at 750 °C for the $LaCoO_3$ from 6 to 20 h yields a single phase of the perovskite, but reduces considerably the BET surface, thus decreasing the activity of the catalyst (Table 2).

Partial substitution of lanthanum in the perovskite with palladium (fresh catalyst) decreases the T_{10} and T_{50} values by 55° as compared to the $LaCoO_3$ catalyst. The T_{90} value becomes lower by 45°. The enhancement of catalytic activity may be attributed both to the slightly higher BET surface of the perovskite used and to the presence of palladium. The substitution of 10% of the lanthanum in the $LaCoO_3$ perovskite with silver also enhances methane conversion, despite the smaller decrease of the T_{10} and T_{50} values. After 500 h on stream during methane combustion, all the catalysts tested suffered a decrease in activity. And, again, the values of T_{10}, T_{50} and T_{90} obtained over $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ were lower (Table 2) than those attained over $LaCoO_3$ after 500 h on stream. The difference is particularly distinct with T_{90}, because in the presence of $LaCoO_3$ 90% conversion was not achieved until the temperature rose to 780 °C. This indicates that a partial substitution of La with Ag or Pd in the perovskite increases the activity of the $LaCoO_3$ catalyst.

Table 2
Comparison of methane combustion over monolithic catalysts with $LaCoO_3$, $La_{0.9}Ag_{0.1}CoO_3$ or $La_{0.92}Pd_{0.08}CoO_3$ as active phase

Composition of active phase	Catalytic activity in terms of conversion temperature (°C)			BET (m^2/g)
	T_{10}	T_{50}	T_{90}	
$LaCoO_3$ calcination at 750 °C for 6 h				
Fresh state	465	615	695	10.8
After 500 h on stream	560	668	>780	–
$LaCoO_3$ calcination at 750 °C for 20 h				
Fresh state	560	665	750	5.6
$La_{0.9}Ag_{0.1}CoO_3$				
Fresh state	460	585	650	8.1
After 500 h on stream	520	610	690	–
$La_{0.92}Pd_{0.08}CoO_3$				
Fresh state	410	560	650	11.6
After 500 h on stream	530	635	700	–

The results of stability tests (which involved over 500 h of methane combustion, in the presence of monolithic catalysts with $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ active layers) are plotted in Fig. 5. With the $La_{0.92}Pd_{0.08}CoO_3$ catalysts (Fig. 5(2)), there is a slight but continual decrease in the efficiency of methane conversion with reaction time, in spite of the increased Pd amount on the catalyst surface detected by XPS examinations. The reduced catalytic activity may be associated with the increase in the average oxidation state of Pd also revealed in XPS analysis. After the run at 704 °C, the efficiency of methane conversion decreased from 96.6 to 93.2%. During the run, neither NO_x nor CO were formed. The performance of the catalyst was stable, and the decrease in the extent of methane conversion can be regarded as negligible.

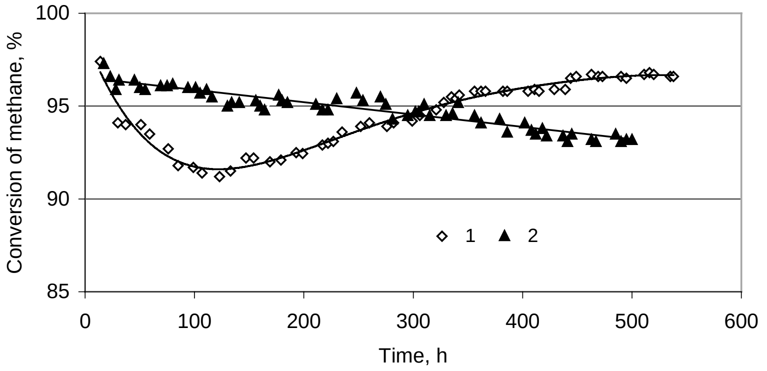

Fig. 5. Efficiency of methane conversion related to reaction time over two monolithic perovskite catalysts: $La_{0.9}Ag_{0.1}CoO_3$ perovskite at reaction temperature 750 °C (1), $La_{0.92}Pd_{0.08}CoO_3$ perovskite at reaction temperature 704 °C (2). Space velocity: $4500\,h^{-1}$; methane concentration: 1% in air.

The $La_{0.9}Ag_{0.1}CoO_3$ catalyst followed a different behavioral pattern during the reaction of methane combustion at 750 °C (Fig. 5(1)). Within the first 133 h of the run, the efficiency of methane conversion decreased from 97.4 to 91.5%, and the maximum carbon oxide concentration in the gas effluent totaled 5 ppm. After 540 h of the run, the efficiency of methane combustion rose to 96.6% and CO content in the gas dropped to 2 ppm. Nitrogen oxides were absent in the gas effluent from methane combustion. The changes in the extent of methane conversion during the run were possibly produced by the considerable differences in the composition of the active layer between the fresh catalyst and the catalyst after the run, as it can be inferred from XPS examinations. After 500 h on stream, the amount of the carbonate groups, which may reduce catalytic activity [25], decreased noticeably, and there was a complete transition of the active phase into the perovskite, as detected by XRD. The increase in catalytic activity to 96.6% during the run might have been contributed by the oxidation of the metallic silver to Ag^+ and by its building-in into the perovskite structure. The small difference between the efficiencies of methane conversion over a fresh catalyst and a catalyst after 500 h of performance indicates that the activity of the mixture including $LaCoO_3$, $La_4Co_3O_{10}$, $AgCoO_2$ and metallic silver is similar to the activity of the perovskite ($La_{0.9}Ag_{0.1}CoO_3$) formed during the run. Since the active layer of the catalyst was not analyzed for composition after 133 h on stream, when catalytic activity was the lowest, it is impossible to tell what exactly contributed to the decrease in the efficiency of methane conversion over this catalyst.

4. Conclusions

XPS analyses show that during 500 h of run the surface composition of monolithic catalysts with $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ as active phases undergoes considerable changes. On the surface of the $La_{0.92}Pd_{0.08}CoO_3$ catalyst, the amount of palladium increases, and so does the average oxidation state of Pd. On the surface of the catalyst with $La_{0.9}Ag_{0.1}CoO_3$ as the active phase, the quantity of the Ag component decreases, and silver undergoes transition from the inactive metallic state into the cation Ag^+, probably built-in into the perovskite structure.

Partial substitution of lanthanum with palladium or silver in the $LaCoO_3$ perovskite enhances the activity of the monolithic catalyst in the combustion of methane.

Monolithic $La_{0.9}Ag_{0.1}CoO_3$ and $La_{0.92}Pd_{0.08}CoO_3$ catalysts display a high activity and a good stability during methane combustion for about 500 h.

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