

BARBARA KUCHARCZYK*, JERZY ZABRZESKI*

MONOLITHIC $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ AND $\text{LaMn}_{1-x}\text{Pt}_x\text{O}_3$ PEROVSKITE CATALYSTS FOR THE OXIDATION OF METHANE AND CARBON OXIDE

The substitution of 0.1–0.2 mol of lanthanum in LaMnO_3 by platinum enhances the activity of the perovskite in CO oxidation, and the $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ -based catalyst was found to be most active in this process. When the CO oxidation involves the temperatures higher than 270 °C, the catalysts based on $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$, $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$ and $\text{La}_{0.85}\text{Pt}_{0.15}\text{MnO}_3$ perovskites do not differ in activity. In CH_4 combustion, the $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ and $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ catalysts display a higher activity than the LaMnO_3 catalyst does. When the Pt content in LaMnO_3 is higher than 0.1, its activity in CH_4 combustion and the resistance to thermal shocks decrease. When some part of La in the LaMnO_3 perovskite is substituted by Pt, the specific surface area of the perovskite decreases from 8.6 m^2/g (LaMnO_3) to 3.1 m^2/g ($\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$).

1. INTRODUCTION

Of the noble metals, Pd, Pt and Au display the highest activity in CH_4 and CO combustion [1]–[2]. Perovskite oxides of the generalized formula ABO_3 show good catalytic activity in these processes and a high thermal resistance. Catalytic activity is ascribed to the metal in position B, while the ion in position A is responsible for the thermal resistance of the catalyst [3]–[5]. LaBO_3 perovskites with Mn, Fe, Co, Ni or Cr as metal B are also efficient catalysts for CH_4 and CO oxidation. Their activity decreases in the following sequence: $\text{LaCoO}_3 > \text{LaMnO}_3 > \text{LaNiO}_3 > \text{LaFeO}_3$, LaCrO_3 [3], [5] and depends on the method of perovskite preparation. Also perovskites of AFeO_3 type with La, Nd or Sm as metal A are active catalysts for the oxidation of CH_4 and CO [4].

Partial substitution of the metal in position A or B by a metal of a different valence changes the structure of the perovskite and enhances its activity [5]–[8]. Promising results are obtained by substituting the metal in position A by Ag [5]–[6] or the

* Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: barbara.kucharczyk@pwr.wroc.pl

metal in position B by Pt or Pd [7]–[9]. The research into the effect of a partial substitution of La in LaMnO₃ by Ce, Sr or Ag has revealed that the activity of each of them in CO and CH₄ oxidation decreases in the order Ag>Ce>Sr>La and is the highest when 0.3 mol of La has been substituted (La_{0.7}M_{0.3}MnO₃) [5]. The activity of the perovskite in the oxidation of hydrocarbons and CO can be enhanced by Pd deposition onto its surface (Pd/La_{0.9}Ce_{0.1}Co_{0.4}Fe_{0.6}O₃, Pd/LaFe_{0.08}Co_{0.2}O₃) [6]–[7] or by partial substitution of Fe by Pd (LaFe_{0.77}Co_{0.17}Pd_{0.06}O₃) [7]. A high activity in CH₄ and CO oxidation can also be achieved when Pd or Pt is deposited onto the surface of hexaalumina (LaAl₁₁O₁₈ or LaMnAl₁₁O₁₉) [8].

2. METHODS OF CATALYST PREPARATION AND EXAMINATION

Monolithic catalysts were prepared on supports made of heat-resisting 00H20J5 foils. The supports were cylindrical in shape (70 mm in length and 26 mm in diameter). They had a honeycomb cross-section of a density of 112 channels/cm² and a wall thickness of 0.05 mm. The support was washcoated with Al₂O₃–TiO₂–La₂O₃ using the sol–gel method. The quantity of the washcoat was 2 wt.% in relation to the support mass. The oxides of perovskite type, LaMnO₃, La_{1–x}Pt_xMnO₃ ($x = 0.05–0.2$) or LaMn_{0.9}Pt_{0.1}O₃, were obtained by mixing appropriate amounts of La(NO₃)₃·6H₂O, Mn(NO₃)₂·4H₂O and H₂PtCl₆. The mixtures were dried at 120 °C and calcined for 6 h at 750 °C. The active layer was deposited by immersing the support in the suspension of an appropriate perovskite in citric acid. The catalysts were calcined at 500 °C for 3 h. The catalysts and perovskites are characterized in the table.

Table

Characterization of La_{1–x}Pt_xMnO₃ ($x = 0.05–0.2$) and LaMn_{0.9}Pt_{0.1}O₃ perovskites

Composition of active phase	Amount of active phase (%)	SSA of perovskite powders (m ² /g _{perovskite})	Mean pore diameter (nm)	Micropore surface area (m ² /g)
LaMnO ₃	14.6	8.58	35	0.95
La _{0.95} Pt _{0.05} MnO ₃	13.2	7.72	30	0.30
La _{0.9} Pt _{0.1} MnO ₃	12.2	3.89	15; 60	0.84
La _{0.85} Pt _{0.15} MnO ₃	14.2	3.93	30	0.27
La _{0.8} Pt _{0.2} MnO ₃	12.2	3.10	30	0.33
LaMn _{0.9} Pt _{0.1} O ₃	13.2	3.15	38	0.72

BET specific surface areas (SSA) were determined from the nitrogen sorption isotherms measured by the static volumetric method at liquid nitrogen temperature, using an Autosorb-1-C/TCD instrument. Pore distribution values were determined from the desorption isotherm, using the BJH (Barrett, Joyner, Halenda) method.

The catalyst samples were tested for their resistance to thermal shocks by passing them through 4000 cycles of heating to 1000 °C and cooling to room temperature. Heat resistance was expressed as the relative change in the mass of the catalysts, calculated as the ratio of the mass change in the catalyst after a certain number of cycles to the initial total mass of the catalyst.

Oxidation was carried out in a laboratory flow reactor placed in a heater (heating ramp: 3 °/min). Activity tests involved combustion of 1 vol. % CH_4 or 1 vol. % CO in air over monolithic perovskite catalysts of a 37.15 cm^3 volume. The hourly space velocity of total gas was fixed at 5800 h^{-1} for CH_4 and at 10,000 h^{-1} for CO. A Sniffer analyzer (Bacharach) was used to measure CH_4 concentration; that of CO was measured with a Monoxor II analyzer (Bacharach) and an automotive emission analyzer MEXA-574GE.

3. RESULTS AND DISCUSSION

When the amount of La substituted by Pt increased, the SSA of the perovskites decreased from 8.6 m^2/g (LaMnO_3) to 3.1 m^2/g ($\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$) (table). The perovskites were characterized by an isotherm of type III in the classification of Brunauer, Deming, and Deming and Teller, as well as by a small hysteresis loop in the adsorption-desorption curves for nitrogen. No hysteresis loops have been detected for the $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ and $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ perovskites.

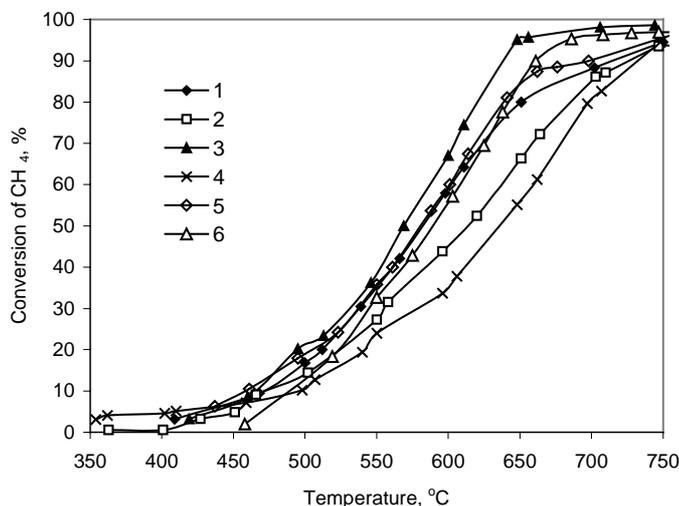


Fig. 1. Methane conversion as a function of temperature for $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ and $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ catalysts. Catalysts: 1 – $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$, 2 – $\text{La}_{0.85}\text{Pt}_{0.15}\text{MnO}_3$, 3 – $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$, 4 – $\text{La}_{0.95}\text{Pt}_{0.05}\text{MnO}_3$, 5 – LaMnO_3 , 6 – $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$

The monolithic $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ -based catalyst was found to display the highest activity in CH_4 oxidation. The perovskite shows a large micropore surface area ($0.84 \text{ m}^2/\text{g}$) compared to the total BET surface area ($3.89 \text{ m}^2/\text{g}$), and also has macropores averaging 60 nm in size. The activity of the $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ ($x = 0.05, 0.15$ and 0.2) catalysts in CH_4 oxidation did not exceed the activity of the LaMnO_3 catalyst (figure 1). This is due to the considerable decrease in the SSA of the perovskite, which results from the increase in the Pt content (table). When the Pt content is high, residual chlorine from the decomposition of H_2PtCl_6 can persist in the perovskite (XPS). In CH_4 oxidation, the activity of the monolithic $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ catalyst is higher than that of the LaMnO_3 catalyst (at the temperatures higher than $645 \text{ }^\circ\text{C}$) and lower than that of the $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ catalyst (figure 1).

Methane oxidation over perovskite catalysts involves high temperatures (up to $800 \text{ }^\circ\text{C}$). Temperature variations in the course of the process may be responsible for cracking and fall-off of both washcoat and perovskite from the support surface. Tests for the resistance of the $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$ catalysts to alternate heating and cooling have revealed a reduction in the catalyst mass with the increase in the number of heating and cooling cycles. After 4000 cycles the relative change in the mass of the catalysts was -1.2% . With the increase of the Pt content in the perovskite the catalyst resistance to thermal shocks decreased (figure 2).

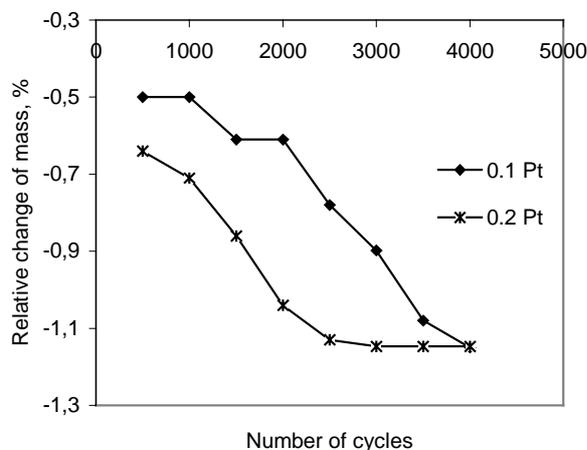


Fig. 2. Resistance of $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ ($x = 0.1$ and 0.2) catalysts to thermal shocks

As for CO oxidation, the activity of the $\text{La}_{0.95}\text{Pt}_{0.05}\text{MnO}_3$ catalyst exceeds that of the LaMnO_3 catalyst only above $260 \text{ }^\circ\text{C}$. $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ ($x = 0.1, 0.15, 0.2$) catalysts display a higher activity compared to that of the LaMnO_3 . The activity of the catalysts was found to decrease when the substitution of La by Pt increased from 0.1 to 0.2 (figure 3). Higher activity of the LaMnO_3 perovskite after partial substitution of La by Pt results

from the presence of Pt, the most active catalyst in CO oxidation. Below 270 °C, the $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ catalyst shows a lower activity in CO oxidation than $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ ($x = 0-0.2$) catalysts. The activity of $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ equals that of the $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$ and $\text{La}_{0.85}\text{Pt}_{0.15}\text{MnO}_3$ catalysts at temperatures exceeding 270 °C (figure 3).

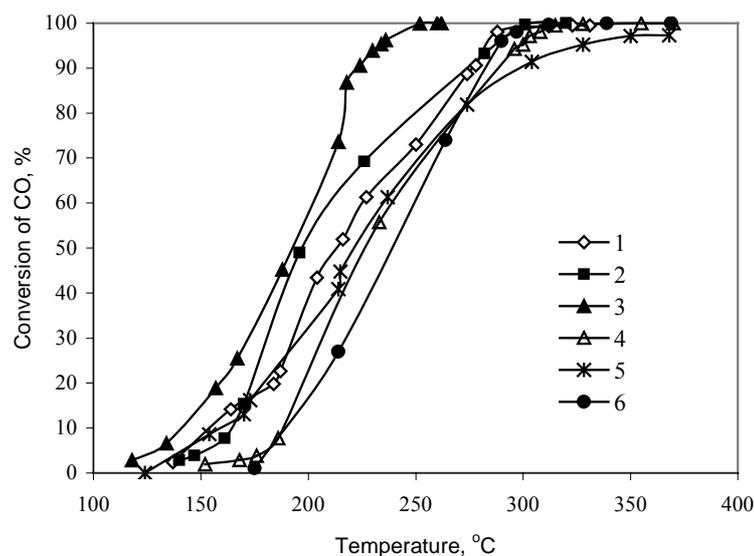


Fig. 3. Oxidation of CO over monolithic $\text{La}_{1-x}\text{Pt}_x\text{MnO}_3$ and $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ catalysts. Catalysts: 1 – $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$, 2 – $\text{La}_{0.85}\text{Pt}_{0.15}\text{MnO}_3$, 3 – $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$, 4 – $\text{La}_{0.95}\text{Pt}_{0.05}\text{MnO}_3$, 5 – LaMnO_3 , 6 – $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$

4. CONCLUSIONS

The substitution of La by Pt in the LaMnO_3 perovskite reduces its SSA from 8.58 m^2/g (LaMnO_3) to 3.1 m^2/g ($\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$).

When 0.1 mol of La in the LaMnO_3 catalyst is substituted by Pt, its activity in CH_4 oxidation increases. If the Pt content is higher than 0.1, this reduces the activity of LaMnO_3 in CH_4 oxidation and its resistance to thermal shocks.

For CO oxidation the substitution of 0.1–0.2 mol of La by Pt in LaMnO_3 enhances the perovskite activity. The $\text{La}_{0.9}\text{Pt}_{0.1}\text{MnO}_3$ catalyst shows the highest activity in this process. The activity of the $\text{LaMn}_{0.9}\text{Pt}_{0.1}\text{O}_3$ catalyst equals that of the $\text{La}_{0.8}\text{Pt}_{0.2}\text{MnO}_3$ and $\text{La}_{0.85}\text{Pt}_{0.15}\text{MnO}_3$ catalysts at temperatures higher than 270 °C.

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REFERENCES

- [1] GELIN P., PRIMET M., *Complete oxidation of methane at low temperature over noble metal based catalyst: a review*, Appl. Catal. B, 2002, Vol. 39, 1.
- [2] MUSIALIK-PIOTROWSKA A., KOYER-GOLKOWSKI A., *Porównanie aktywności katalizatorów perowskitowego i palladowego w utlenianiu organicznych zanieczyszczeń powietrza*, Ochrona Środowiska, 2002, 2(85), 7.
- [3] CIMINO S., PIRONE R., LISI L., *Zirconia supported LaMnO₃ monoliths for the catalytic combustion of methane*, Appl. Catal. B: Environ., 2002, Vol. 35, 243.
- [4] CIAMBELLI P., CISINO S., ROSSI S., LISI L., MINELLI G., PORTA P., RUSSO G., *AFeO₃ (A = La, Nd, Sm) and LaFe_{1-x}Mg_xO₃ perovskites as methane combustion and CO oxidation catalysts: structural, redox and catalytic properties*, Appl. Catal. B, 2001, Vol. 29, 239.
- [5] SONG K., CUI H.X., KIM S.D., KANG S., *Catalytic combustion of CH₄ and CO on La_{1-x}M_xMnO₃ perovskites*, Catal. Today, 1999, Vol. 47, 155.
- [6] TANAKA H., MIZUNO N., MISONO M., *Catalytic activity and structural stability of La_{0.9}Ce_{0.1}Co_{1-x}Fe_xO₃ perovskite catalysts for automotive emissions control*, Appl. Catal. A, 2003, Vol. 244, 371.
- [7] ZHOU K., CHEN H., TIAN Q., HAO Z., SHEN D., XU X., *Pd-containing perovskite-type oxides used for three-way catalysts*, J. Mol. Catal. A., 2002, Vol. 189, 23.
- [8] POCOROBA E., JOHANSSON E.M., JARAS S.G., *Ageing of palladium, platinum and manganese-based combustion catalysts for biogas applications*, Catal. Today, 2000, Vol. 59, 179.

MONOLITYCZNE KATALIZATORY PEROWSKITOWE LaMnO₃
Z DODATKIEM PLATYNY W UTLENIANIU METANU I MONOTLENKU WĘGLA

Jeśli w perowskicie LaMnO₃ zastąpić od 0,1 do 0,2 mola lantanu platyną, to zwiększa się aktywność tego perowskitu w utlenianiu CO. Najwyższą aktywność w utlenianiu wykazuje katalizator z perowskitem La_{0,9}Pt_{0,1}MnO₃. Metan jest efektywniej utlaniany, gdy 0,1 mola lantanu w katalizatorze LaMnO₃ zastępuje się platyną. Większa zawartość platyny w perowskicie LaMnO₃ obniża zarówno jego aktywność w utlenianiu CO, jak i odporność katalizatora perowskitowego na naprzemienne zmiany temperatury. Zastąpienie części lantanu w perowskicie LaMnO₃ platyną zmniejsza powierzchnię właściwą perowskitu z 8,58 m²/g (LaMnO₃) do 3,1 m²/g (La_{0,8}Pt_{0,2}MnO₃).