

## Complete oxidation of methane on Pd-substituted perovskite $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$

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B-site substituted perovskite compounds  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  were synthesized by urea-assisted combustion method and considered for further application as catalysts for methane combustion. Palladium substitution for copper in terms of effect on catalyst structural and physicochemical properties has been investigated by using X-ray diffraction (XRD), low-temperature adsorption of nitrogen (BET), and scanning electron microscopy (SEM). Results showed that incorporation of palladium into perovskite crystal structure brings about a material of high thermal stability and improved catalytic properties compared with non-substituted  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ .

**Keywords:** perovskite, Pd-substituted perovskite, methane catalytic oxidation, XRD, SEM, BET.

### INTRODUCTION

Methane accounts for 14% of the total amount of greenhouse gas (GHG) emissions originating from mines, agriculture, and gas facilities [1]. There are some considerations for assessing a new value for methane global warming potential (GWP). The Environmental Protection Agency (EPA) recently proposed raising methane's GWP value from 21 to 25 [2]. The European Union (EU) tackles methane emissions together with other GHG emissions, planning a reduction in the EU's greenhouse gas emissions by 20% in 2020 compared to 1990 [2]. The emission of methane can be used as a fuel in combustion processes as well as in thermal and catalytic reverse flow reactors, catalytic monolith combustors, catalytic lean burn gas turbines, recuperative gas turbines, or concentrators [3]. Neutralization of gases containing methane can be realized by variety of methods, one of them being the complete catalytic oxidation [4,5]. In the case of complete oxidation of methane, palladium and platinum are the most widely used metals because of their high activity [6–9]. It was found that Pd is more active than Pt for methane oxidation, and most of the research works have concentrated on Pd as the active component in recent years. Most studies have primarily focused on the use of alumina as the supporting material for Pd-based catalysts [7–10], and these studies have shown that the activity of each catalyst is influenced by many factors, e.g.

precursor, support, Pd loading, calcination temperature, morphology of the Pd crystallites, catalyst pretreatment procedure, and reaction conditions. The main disadvantage of Pd catalysts is their instability and high price. In recent years, a lot of research effort has been focused on the synthesis of perovskite-type oxides as possible catalysts in the process of catalytic combustion [11]. Perovskites are characterized by a general  $\text{ABO}_3$  structure and remarkable heat resistance [11,12]. The perovskites can be modified in terms of non-stoichiometry and partial substitution by varying the types of atoms at the A and B sites thus providing an opportunity to prepare different perovskites with possible application as catalysts in the reaction of complete oxidation of methane. Since the type of B-site cations determines the catalytic properties of perovskite-type oxides, the B-site substitution of perovskites was considered an effective way to modify their catalytic properties due to generation of new lattice defects, mixed valence states, and nonstoichiometric oxygen.

The aim of the present study was to investigate the effect of introducing a noble metal into the perovskite structure as a low-level substituting element. B-site substituted perovskites,  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$ , obtained by urea-assisted combustion synthesis, were selected and investigated for further application as catalysts in methane combustion.

### EXPERIMENTAL

$\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  samples were synthesized by solution-combustion

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method using a stoichiometric mixture of the corresponding metal nitrates as oxidizers and urea as fuel. Initial compounds were dissolved in appropriate amount of distilled water. The clear solution was evaporated on a laboratory heater. After evaporation a self-initialized ignition process occurred. Combustion resulted in a fine powder residue. The sample  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  was thermally treated at  $550^\circ\text{C}$  for 30 min., after that at  $750^\circ\text{C}$  for 1 h, and finally treated at  $1100^\circ\text{C}$  for 5 h. The  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  sample was thermally treated at  $550^\circ\text{C}$  for 30 min, then at  $750^\circ\text{C}$  for 1 h, and finally at  $1100^\circ\text{C}$  for 2 h. Palladium substitution for Cu with reference to influence on structure and morphology was studied using X-ray diffraction of Bruker D8 Advance with Cu  $K\alpha$  radiation and LynxEye detector. Powder diffraction patterns were collected between 10 and 120 degrees  $2\theta$  with a step of 0.02 degree  $2\theta$  and counting time 175 s/step. Phase identification was performed by Diffracplus EVA using ICDD-PDF2 database. The mean crystallite size was determined based on all peaks within recorded powder patterns using whole powder pattern fitting with Topas-4.2 software package and fundamental parameters of the peak shape description including appropriate corrections for instrumental broadening and diffractometer geometry. Rietveld refinement of the structural parameters was performed with Topas 4.2.

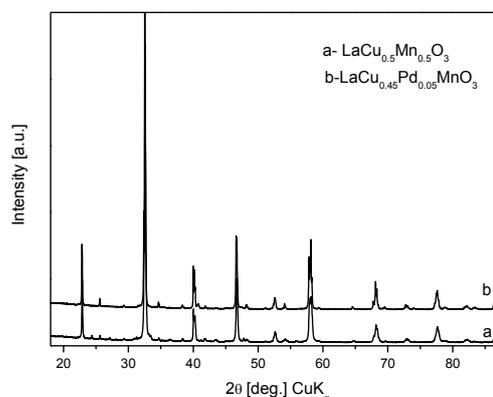
Specific surface area of the catalyst samples ( $S_{\text{BET}}$ ) was determined by low-temperature adsorption of nitrogen according to the BET method using a Quantachrome NOVA 1200 apparatus.  $S_{\text{BET}}$  was calculated applying the Brunauer, Emmet and Teller (BET) equation for  $\text{N}_2$  relative pressure within the range of  $0.05 < P/P_0 < 0.30$ .

Elemental composition as well as morphology and microstructure of the catalysts were studied by a JEOL-JSM-6390 scanning electron microscope equipped with energy dispersion spectroscopy (EDS) with (Li, Si) detector.

Catalytic activity tests were carried out by means of a CATLAB Hiden Analytical apparatus equipped with a mass-spectrometer in a continuous-flow type quartz-glass reactor at atmospheric pressure. The following testing conditions were applied: catalyst bed volume of  $0.5 \text{ cm}^3$ , irregular shaped particles of 0.7-mm average diameter, and inner reactor diameter of 7.0 mm ( $D_{\text{reactor}}/D_{\text{particles}} \approx 10$ ). The gaseous hourly space velocity (GHSV) was fixed at  $12000 \text{ h}^{-1}$ . Water vapour effect on the methane combustion was also investigated.

## RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  samples heated at  $1100^\circ\text{C}$ . Both patterns show diffraction peaks corresponding to the perovskite structure displayed by both samples. For both samples heated at  $500^\circ\text{C}$ , XRD analysis indicates formation of a  $\text{La}_2\text{CuO}_4$  impurity phase. After thermal treatment of the  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  sample at  $750^\circ\text{C}$  the amount of  $\text{La}_2\text{CuO}_4$  phase is decreased. Upon further heating at  $1100^\circ\text{C}$ , the  $\text{La}_2\text{CuO}_4$  phase disappears completely. In  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$ , the amount of  $\text{La}_2\text{CuO}_4$  phase was very small even after heating at a temperature of  $750^\circ\text{C}$ . This fact indicates that the presence of Pd suppresses the formation of  $\text{La}_2\text{CuO}_4$  phase in favour of the perovskite phase.



**Fig. 1.** XRD patterns of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  heated at  $1100^\circ\text{C}$

Powder diffraction patterns of both samples heated at  $1100^\circ\text{C}$  can be indexed in orthorhombic space group Pbnm with very close unit cell parameters. A Rietveld structure refinement was performed. Refined parameters were unit cell parameters, line profile parameters, zero shifts, background parameters, positional parameters, occupancy, and thermal displacement parameters of ions in the structure. Preferred orientation effects were not included. Results of the structure refinement are shown in tables 1 and 2. The present results show systematic changes in unit cell parameters after doping with Pd. The polyhedral crystal structure of orthorhombic perovskite is presented in figure 2.

A calculation of cell deformation index was performed by using the following equation:  $ap = (a/\sqrt{2} + b/\sqrt{2} + c/2)/3$  [13]. An estimate of polyhedron deformation parameter was carried out through the equation:  $\Delta = \sum[(r_i - r)/r]/n \times 10^3$ , where  $r$  is the individual bond length (A–O or B–O), and  $n$

is the number of bonds [14]. The results are presented in Table 3. It is seen that palladium introduction to the perovskite structure decreases the deformation level, thus stabilizing the structure.

Elemental analysis results for a sample of nominal composition  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  are presented in table 4, while table 5 gives data on a sample of nominal composition  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$ . Obviously, the experimental elemental composition

of both samples is close to the corresponding nominal composition.

Fig. 3 shows SEM images of the samples at different magnifications. It is seen that the  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  sample is a ceramic material with smooth surface, while  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  is a material containing particles with well-developed porous surface.

**Table 1.** Crystal structure data on  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  SG. Pbnm  $a = 5.5225(1)$  (Å),  $b = 5.4800(1)$  (Å),  $c = 7.7680(2)$  (Å)

Site	N	x	y	z	Occ	Bizo
A	4	0.0002(7)	0.5192(2)	1/4	(La+3) 1	0.94(2)
B	4	0	0	0	(Mn+4) 0.5 (Cu+2) 0.5	0.51(3) 0.51(3)
O1	4	-0.078(2)	0.003(2)	1/4	(O-2) 1	1.3(1)
O2	8	0.220(2)	0.289(2)	0.022(1)	(O-2) 1	1.3(1)

**Table 2.** Crystal structure data on  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  SG. Pbnm  $a = 5.52702(5)$  (Å),  $b = 5.48809(6)$  (Å),  $c = 7.77305(8)$  (Å)

Site	N	x	y	z	Occ	Bizo
A	4	0.0029(4)	0.5224(1)	1/4	(La+3) 1	0.68(2)
B	4	0	0	0	(Mn+4) 0.5 (Cu+2) 0.45 (Pd+2) 0.05	0.67(3) 0.67(3) 0.67(3)
O1	4	0.084(2)	0.002(2)	1/4	(O-2) 1	1.1(1)
O2	8	0.226(2)	0.271(2)	0.030(1)	(O-2) 1	1.1(1)

**Table 3.** Structure deformation indicators

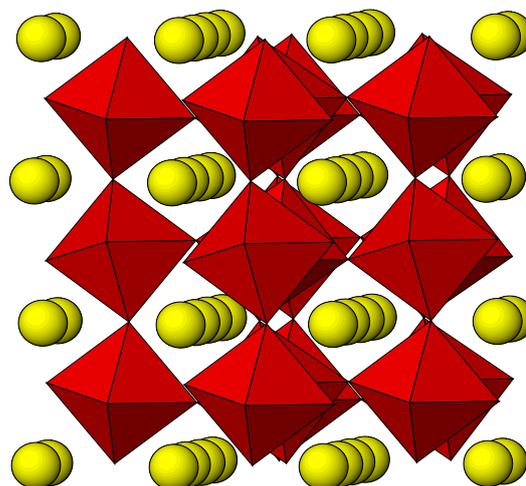
	$\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$	$\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$
cell deformation index	4.75	4.13
deformation of octahedron	0.2158	0.0799

**Table 4.** Theoretical and experimental atomic percentage of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$

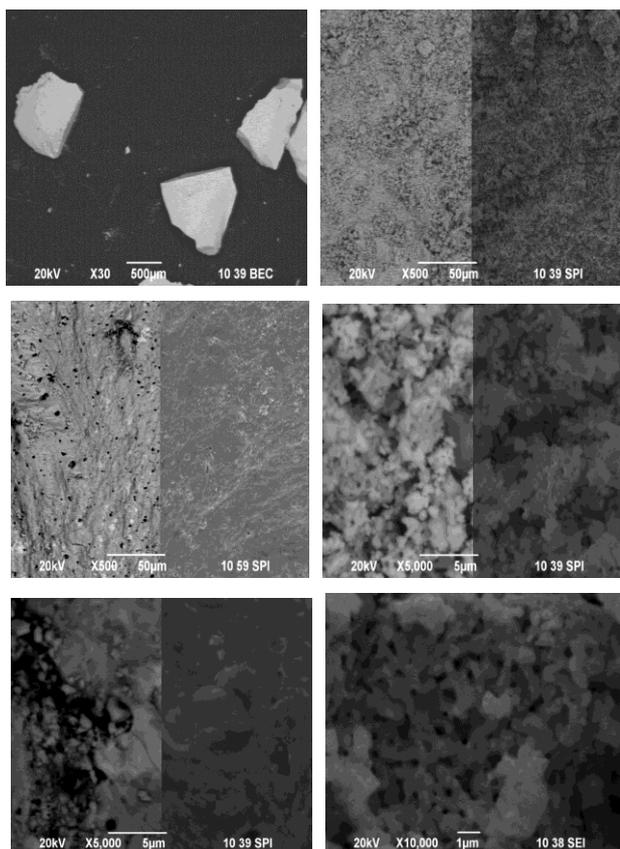
Atomic %	La	Cu	Mn	O
teoretical	20	10	10	60
experimental	20.35	10.61	9.25	61.13

**Table 5.** Theoretical and experimental atomic percentage of  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$

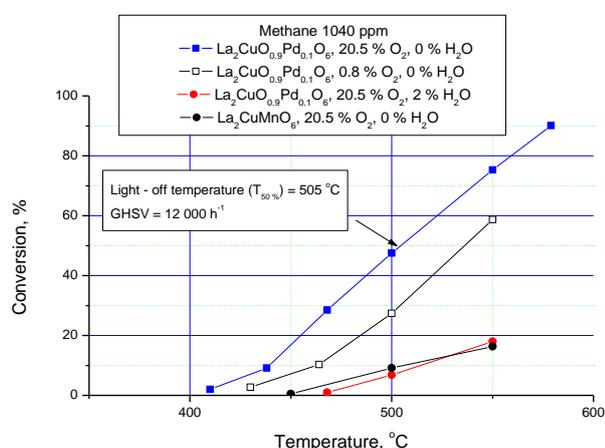
Atomic %	La	Cu	Pd	Mn	O
teoretical	20	9	1	10	60
experimental	24.65	9.91	0.99	10.93	55.52



**Fig. 2.** Polyhedral presentation of the crystal structure of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ : octahedra –  $\text{MO}_6$ , bals –  $\text{La}^{3+}$  ions



**Fig. 3.** SEM photograph images of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  (left column) and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  (right column) at different magnifications.



**Fig. 4.** Catalytic activities of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  in reaction of complete oxidation of methane.

Figure 4 displays comparative results of the catalytic activities of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  samples in the reaction of complete methane oxidation. Evidently, the catalytic activity of  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  is higher than that of  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ . This fact cannot only be explained by a difference in specific surface area ( $0.6 \text{ m}^2 \cdot \text{g}^{-1}$  and  $0.2 \text{ m}^2 \cdot \text{g}^{-1}$ , respectively). Calculated

values for the rate constants at  $500^\circ\text{C}$  show a ratio of 6.8:1 in favour of the palladium containing catalyst. As the observed activation energies (assuming first-order kinetics) for both samples have almost the same values ( $\sim 105 \text{ kJ} \cdot \text{mol}^{-1}$ ), this fact gives an opportunity to compare the pre-exponential factors (10.2:1). It is seen that water vapour has an inhibition effect on the Pd-containing sample. The reaction rate is also dependent on oxygen content in the gas phase thus revealing a more complicated reaction mechanism than that described by simple first-order kinetics.

## CONCLUSIONS

Urea-assisted combustion synthesis was proved an appropriate method for synthesis of B-site substituted perovskite compounds. Palladium substitution for copper has influence on the structural and physicochemical properties of the catalysts demonstrating that Pd incorporation into perovskite crystal structure gives rise to a material of high thermal stability and bettered catalytic properties compared with non-substituted  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ .

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ПЪЛНО ОКИСЛЕНИЕ НА МЕТАН ВЪРХУ ЗАМЕСТЕН С ПАЛАДИЙ ПЕРОВСКИТ  
 $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$

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(Резюме)

За получаване на Б-катионно заместени перовскитови състави  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  и  $\text{LaCu}_{0.45}\text{Pd}_{0.05}\text{Mn}_{0.5}\text{O}_3$  бе използван метода синтез чрез изгаряне от разтвор с използване на гориво урея с оглед възможното им приложение като катализатори за изгаряне на метан. Влиянието на заместването на Cu с Pd върху физико-химичните свойства на катализаторите беше изследвано с помощта на прахова рентгенова дифракция (РД), нискотемпературна адсорбция на азот (БЕТ) и сканираща електронна микроскопия (SEM). Резултатите за влиянието на паладия при заместването на Cu показват, че включването на Pd в кристалната структура води до получаване на материал с по-висока термична стабилност и с подобрени каталитични свойства в сравнение с  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ .