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# Noble metal-doped perovskites for the oxidation of organic air pollutants

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**Abstract**

Ag-Pt- and Pd-doped $LaMnO_3$-based perovskite catalysts were prepared and their activity in the oxidation of toluene, *n*-heptane and ethanol was investigated. The activity of $LaMnO_3$-based catalyst was very high in the oxidation of each compound tested. The Ag-doped catalyst was the most active in the oxidation of each compound and it displayed the highest BET specific surface area (SSA) also. The influence of Pt or Pd doping on perovskite activity is negligibly small. Pt-doped catalysts are slightly more active while Pd-doped catalysts are slightly less active than the pure perovskite. Thermogravimetric-differential thermal analysis (TG-DTA) for the catalyst precursor indicates that above 500 °C a perovskite structure began to form. The XRD analysis reveals the presence of the $LaMnO_{3.15}$ perovskite phase and, additionally, the presence of some metal oxide phases (e.g. $La_2O_2CO_3$, $Mn_2O_3$) and carbon. BET SSA measured after the oxidation tests was found to decrease for each catalyst. There was no relation between the chemical composition of the catalyst and the loss of SSA.

*Keywords:* Air pollution; Catalyst; Perovskite; Oxidation; VOC

## 1. Introduction

Catalytic oxidation is an efficient and economical method for the abatement of organic air pollutants emitted with industrial waste gases. Noble metal catalysts (Pt, Pd) are widely used in such processes. The search for cheaper substitutes of noble metals has led to the study of the catalytic properties of mixed metal oxides, typically oxides of Cr, Mn, Co or Cu. Of the metal oxide catalysts, perovskites of a structure formula $ABO_3$ (where position A is chosen for rare earth metals and position B for transition metals) have been widely proposed as alternative catalysts for the deep oxidation of volatile organic compounds (VOCs). It has been reported that the perovskites of a $LaMO_3$ structural formula, with M = Mn, Co or Ni, are particularly suited for total VOC oxidation. A partial substitution of ions in position A and/or position B for $A'$ and $B'$ produces crystal lattice defects or creates $O^{2-}$ vacancies in the lattice, thus enhancing the catalytic properties of such catalysts [1–3]. Doping with Ag atoms, particularly in combination with manganese oxides, improves the activity of metal oxide catalysts for greater oxygen storage and mobility [4]. Generally, metal oxides, including perovskites, highly active in oxygenate oxidation, have been found to be less active than noble metals in the oxidation of hydrocarbons, particularly aromatics. Partial substitution of La with Ag atoms in the $La_{1-x}Ag_xMnO_3$ perovskite (where $x = 0.2$–$0.25$ at.) has resulted in the enhancement of catalyst activity in the oxidation of a variety of VOCs, including aromatic hydrocarbons [5,6].

In recent years, perovskites have been investigated extensively as potential three-way catalysts for automotive exhaust gas purification. The incorporation of noble metals (Pt, Pd, Rh) into a perovskite structure not only enhances the activity of the catalyst but also stabilizes the metal against sintering, metal-support interaction and volatilization. Even small amounts of noble metals, mainly substituted in position B, increases the activity and selectivity of perovskites in exhaust cleaning processes. Investigations into Pd-doped perovskites have led to the conclusion that owing to the changes in the automotive exhaust atmospheres and temperatures, metallic Pd particles can be dispersed in the form of ions in the perovskite crystal, thus enabling an automotive catalyst to regenerate by itself (an intelligent catalyst) [7,8].

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Our earlier investigations into the activity of $LaMnO_3$ perovskites doped with silver or platinum have shown that such catalysts display a high activity in the oxidation of typical VOCs differing in chemical structure [9,10]. The aim of the present study was to prepare by a new method $LaMnO_{3+\delta}$-based perovskite catalysts doped with noble metals (Ag, Pt or Pd) and to investigate their activity in the oxidation of VOCs representing typical organic air pollutants.

## 2. Experimental

### 2.1. Catalyst preparation

For the purpose of the study, four $LaMnO_3$-based catalysts doped with platinum were manufactured (containing 0.02, 0.1, 0.2 and 0.5 wt.%), two catalysts doped with palladium (0.1 and 0.5 wt.%) and one doped with silver ($La_{0.75}Ag_{0.25}MnO_3$). The La–Mn perovskite precursor was manufactured from the aqueous solution of the nitrates of appropriate metals ($La(NO)_3 \cdot 6H_2O$ and $Mn(NO)_3 \cdot 4H_2O$) with ammonium carbonate. The pH of the solution was adjusted to 7–8. The resulting solid was dried at 120 °C for 15 h. The decomposition of the precipitated and dried product to $LaMnO_{3+\delta}$ was followed by TG-DTA investigations with the TG-DTA equipment STA 449 Jupiter from Netzsch GmbH. The Ag-containing perovskite was prepared from the water solution of adequate amounts of the perovskite precursor and $AgNO_3$, dried at 120 °C and calcined at 600 °C for 6 h. Pt- or Pd-doped catalysts were manufactured using adequate amounts of the perovskite precursor, $H_2Pt(OH)_6$ acid or palladium acetate in ethanol solution. After drying at 120 °C for 2 h and calcination at 600 °C for 6 h, all catalyst samples were pressed and sieved to the size of 1.5–2 mm.

### 2.2. Catalyst characterization

The BET specific surface area (SSA) was determined for each of the catalysts, using BET apparatus SA 3100 S of Coulter Electronics Inc. Miami. The measurements were carried out in the 5-point mode. TG-DTA investigations for the perovskite precursor decomposition have been carried out using the TG-DTA equipment STA 449 Jupiter from Netzsch GmbH. Structural examinations of selected catalyst powders have been performed using a Philips MRD-HRD diffractometer, $CuK_{\alpha 1}$ being the radiation source ($\lambda = 0.15406$ nm).

### 2.3. Catalyst activity

For all catalytic experiments an integral reactor of silica (diameter, 11 mm; length, 300 mm) was used. The activity of the manufactured samples was tested in the oxidation of toluene, *n*-heptane and ethanol. The reaction temperature varied from 50 to 450 °C, gas hourly space velocity amounted to 18,000 $h^{-1}$ and the concentration of each compound under oxidation approached 5 $g/m^3$. Catalyst activity was assessed in terms of test compound conversion calculated from the peak area of the compound measured in the gases at the outlet of the reactor and compared to the peak area of the corresponding compound obtained at 55 °C, assuming that at such temperature conversion fails to occur. The concentration of the reaction products was analyzed by a gas chromatograph with FID detection (Agilent 6890 N). The data of the chromatographic column HP-5 were: diameter 530 μm and length 60 m. The temperature of column was programmed from 80 to 140 °C.

## 3. Results and discussion

### 3.1. Results of catalyst characterization

The results of TG-DTA analysis (Fig. 1) showed three mass-change regions for the analyzed material – the first up to 300 °C resulted from the loss of adsorbed water. The strong mass loss region from 320–520 °C was attributed to the decarbonization and dehydratation, processes accompanying the $LaMnO_{3+\delta}$

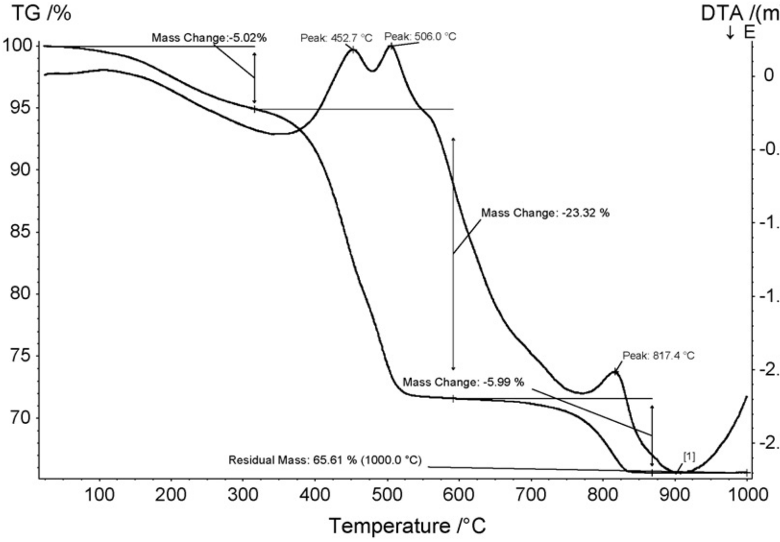

Fig. 1. Combined TG-DTA measurement of a precipitated and dried $LaMnO_3$ precursor.

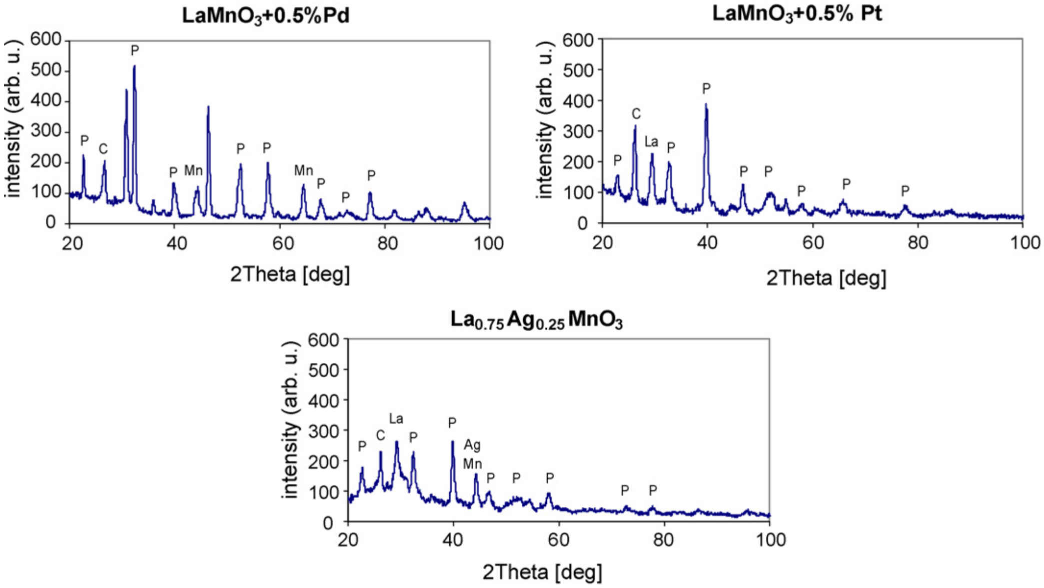

Fig. 2. Results of X-ray analysis of selected catalyst powder samples (P: perovskite, C: carbon, La: $La_2O_2CO_3$, Ag: silver, Mn: $Mn_2O_3$).

perovskite structure formation. The last mass loss (about 6%) came from the final perovskite structure formation.

The XRD patterns of the Pd- (0.5 wt.%), Pt- (0.5 wt.%) and Ag-modified $LaMnO_{3+\delta}$ catalysts are shown in Fig. 2. The XRD measurements are in agreement with the TG-DTA results. All patterns for a $LaMnO_{3.15}$ perovskite were found. The diffraction peaks revealed the presence of the $LaMnO_{3.15}$ perovskite phase (P) and, additionally, the presence of carbon (C), silver (Ag) and some metal oxides phases (e.g. $Mn_2O_3$, $La_2O_2CO_3$). Some amorphous phases can also be distinguished. Additional XRD patterns beside characteristic for $LaMnO_{3+\delta}$ phase, indicating not completely formed perovskite structure, can be found for the perovskite precursors calcined at lower temperatures, e.g. 600 °C were already reported [11,12].

The values of the BET SSAs for fresh and aged catalysts are summarized in Table 1.

As shown by these data, the BET SSA of the samples ranges from 15.96 to 21.98 $m^2/g$. The highest SSA was determined for the Ag-doped catalyst while the lowest one was that for the catalyst containing 0.5 wt.% palladium. BET SSA measured after the oxidation tests was found to decrease for each catalyst. The decrease ranged from 8% for pure perovskite and the perovskite with the lowest platinum content (0.02 wt.%) to 50% for $LaMnO_3$/Pd (0.5 wt.%). There was no relation between the chemical composition of the catalyst and the loss of SSA.

Table 1
Results of BET specific surface area measurement for fresh and used catalysts

| Catalyst | BET surface area of catalyst ($m^2/g$) | |
|---|---|---|
| | Fresh | Used |
| $LaMnO_3$ | 17.54 | 16.07 |
| $La_{0.75}Ag_{0.25}MnO_3$ | 21.98 | 19.75 |
| $LaMnO_3$/0.5% Pt | 17.42 | 11.03 |
| $LaMnO_3$/0.2% Pt | 19.24 | 16.97 |
| $LaMnO_3$/0.1% Pt | 16.82 | 10.77 |
| $LaMnO_3$/0.02% Pt | 19.5 | 17.94 |
| $LaMnO_3$/0.5% Pd | 15.96 | 8.11 |
| $LaMnO_3$/0.1% Pd | 19.17 | 17.28 |

### 3.2. Catalyst activity

The results and temperatures of conversion (50% and 90%) are plotted in Figs. 3 and 4, and summarized in Table 2.

The reactivity of the compounds combusted was the same for all the catalysts tested and decreased in the following sequence: ethanol > *n*-heptane > toluene. The Ag-modified catalyst showed the highest activity in the oxidation of all the test compounds and also displayed the highest BET SSA. 50% conversion of ethanol, *n*-heptane and toluene was obtained at 105, 115 and 140 °C, respectively. The activity of the other catalysts was similar but distinctly lower than that of $La_{0.75}Ag_{0.25}MnO_3$. To achieve a 50% conversion of ethanol and toluene, the reaction temperatures had to be increased by at least 20 °C, and for *n*-heptane even by 40 °C.

The differences in the temperatures of 90% conversion between the VOCs tested were distinctly lower than those of 50% conversion, except for the oxidation of *n*-heptane over the Ag-doped perovskite. For this catalyst, 90% *n*-heptane conversion was achieved at 170 °C, while for the other catalysts such level of conversion required temperatures by 50 °C higher. The temperature of 90% conversion of ethanol varied from 150 °C over $La_{0.75}Ag_{0.25}MnO_3$ to 185 °C over the less active $LaMnO_3$/Pd (0.1 wt.%) catalyst; the temperatures of 90% conversion for toluene ranging from 220 °C over $LaMnO_3$/Pt (0.5 wt.%) to 260 °C over $LaMnO_3$/Pd (0.1 wt.%).

The rank in the catalyst activity depending on temperatures of 50% and 90% test compounds conversion have shown that in all cases the $La_{0.75}Ag_{0.25}MnO_3$ catalyst was the most active one followed by the Pt-doped perovskites. $LaMnO_3$/Pd catalysts were shown only the same catalytic activity than the pure perovskite. The high activity of Ag–Mn oxides in VOCs oxidation for greater oxygen adsorption and mobility has been

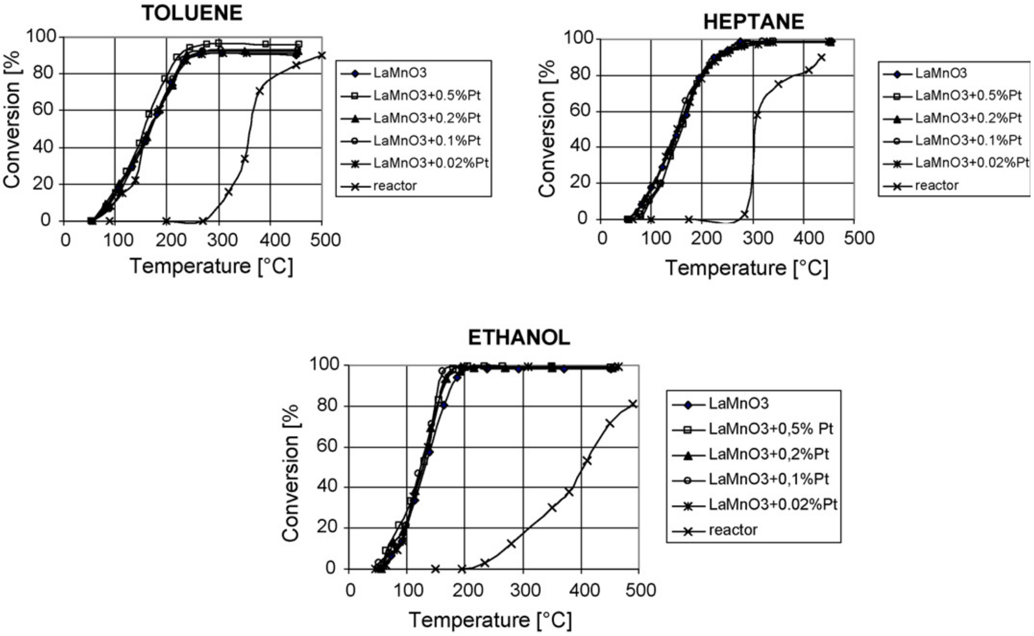

Fig. 3. Conversion of toluene, *n*-heptane and ethanol over Pt-doped perovskite catalysts.

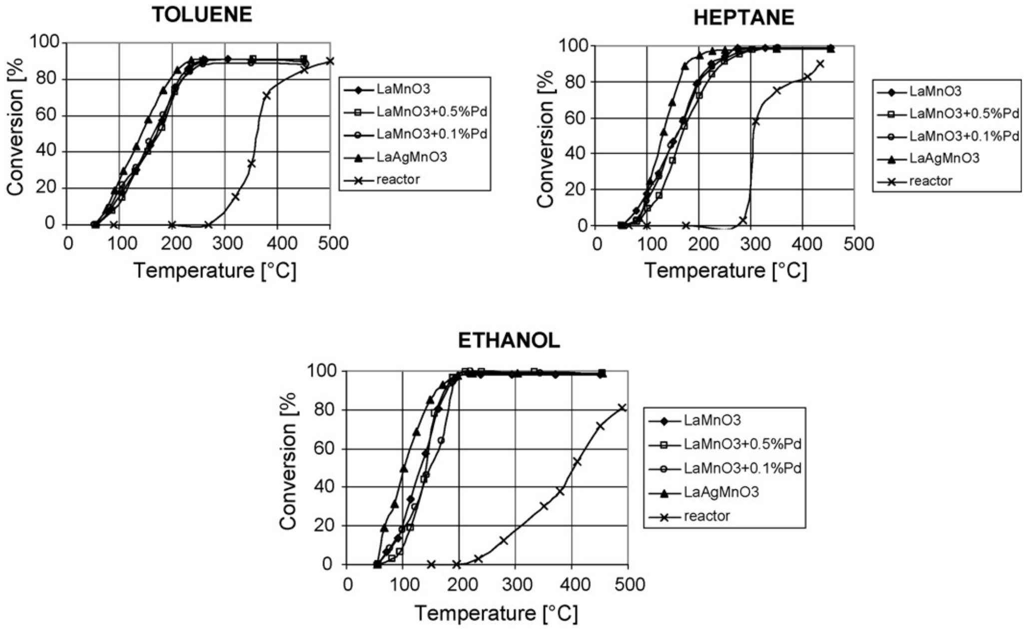

Fig. 4. Conversion of toluene, *n*-heptane and ethanol over Pd- and Ag-doped perovskite catalysts.

Table 2
Temperatures [°C] of 50% and 90% conversion of oxidized compounds

| Catalyst | Ethanol | | *n*-Heptane | | Toluene | |
|---|---|---|---|---|---|---|
| | 50% | 90% | 50% | 90% | 50% | 90% |
| $LaMnO_3$ | 130 | 170 | 150 | 220 | 170 | 250 |
| $La_{0.75}Ag_{0.25}MnO_3$ | 105 | 150 | 115 | 170 | 140 | 230 |
| $LaMnO_3$/0.5% Pt | 130 | 160 | 160 | 220 | 160 | 220 |
| $LaMnO_3$/0.2% Pt | 125 | 160 | 150 | 225 | 170 | 230 |
| $LaMnO_3$/0.1% Pt | 130 | 155 | 150 | 220 | 170 | 230 |
| $LaMnO_3$/0.02% Pt | 125 | 160 | 150 | 220 | 165 | 230 |
| $LaMnO_3$/0.5% Pd | 140 | 170 | 165 | 250 | 175 | 250 |
| $LaMnO_3$/0.1% Pd | 150 | 185 | 155 | 220 | 165 | 260 |

already reported [4]. A similar activity of perovskite alone and doped with Pt or Pd results from the very low addition of noble metals, maximum 0.5 wt.%.

## 4. Conclusions

The catalysts manufactured are active in the oxidation of VOCs differing in chemical structure. The method proposed for the preparation of the perovskite catalysts calcined at temperature of 600 °C only, makes it possible to form the perovskite structure, although some other metallic and metal oxide forms are found as well.

The influence of Pt or Pd doping on perovskite activity is negligibly small. Probably, the content of noble metal, amounting maximum 0.5 wt.%, was too small. Of the catalysts tested, the Ag-doped perovskite ($La_{0.75}Ag_{0.25}MnO_3$) shows the highest activity in the oxidation of each test compound. The same perovskite also displays the highest BET SSA (approx. 22 $m^2$/g). As for the other catalysts, the BET SSA does not exceed 19.5 $m^2$/g. Pt-doped catalysts are slightly more active while Pd-doped catalysts are even slightly less active than the pure perovskite.

Although the preparation method proposed yields active perovskite structures, in the case of Pt- and Pd-doped catalysts, the procedure of mixing the perovskite precursor with $H_2Pt(OH)_6$ or palladium acetate fails to be successful. An enhancement of catalytic activity could probably be expected if the perovskite was used as a support for the noble metal. Our previous investigations have substantiated a high activity of Ag- or Pt-doped perovskite catalysts on $\gamma$-$Al_2O_3$-washcoated, monolithic, metallic supports, using a different method of catalyst preparation [9,10].

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