

# Activity of perovskite catalysts contain Pt or Pd in toluene oxidation

**Agnieszka Borzęcka**

Institute of Environment Protection Engineering, Wrocław University of Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland; e-mail: agnieszka.borzecka@pwr.wroc.pl

Perovskite catalysts with active phase composed of  $\text{LaMnO}_3$  or  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$  doped with noble metals — platinum or palladium — were tested for activity in oxidation of toluene. Their impregnation with solution of Pt or Pd compounds increased the catalytic activity.  $\text{LaMnO}_3$  with Pt content displayed the highest activity.  $\text{LaMnO}_3$  perovskite doped with both noble metals show higher activity than when noble metals were added to  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$  perovskite.

**Keywords:** catalytic VOCs oxidation, perovskite, platinum, palladium.

## Introduction

Volatile organic compounds (VOCs) are dangerous, hazard chemicals present in outdoor and indoor air. They originate mainly from motor vehicle exhausts, combustion processes involving fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes. VOCs are pollutants detrimental to human health, even at very low concentrations. Volatile organic compounds produce also secondary pollutants such as ozone by interacting with nitrogen oxides under sunlight irradiation. Toluene is commonly adopted as a representative of VOCs because it is hard to eliminate.

Techniques such as thermal oxidation, catalytic oxidation, biofiltration, absorption, adsorption, condensation and membrane separation has been developed for the removal of VOCs. The catalytic combustion of VOCs has been considered as one of the most efficient methods to remove VOCs at low concentrations. Compared with incineration, the catalytic oxidation occurs at lower temperatures, thus, decreasing the energy cost and  $\text{NO}_x$  emission.

Precious metals such as platinum, palladium and rhodium have been widely applied to the low temperature complete oxidation. In general, platinum is the most active metal for hydrocarbon combustion and it is widely used supported on alumina. Palladium, which is cheaper than platinum, is also effective for hydrocarbon

combustion. Disadvantages of using noble metals are its thermal stability and cost. To compare, perovskite-type oxides are more thermal stable and cheaper, that causes they are postulated as potential substitutes for noble metals.

Perovskite-type oxides structure of general formula  $\text{ABO}_3$ , with rare earth and alkaline earth ions (La, Ba, Sr, Ca) and transition ions (Cr, Mn, Co, Fe, Ru) respectively in A and B position.

Noble-metal substituted perovskites have been proposed as a new class of catalysts [1, 2]. As was presented in a research by Russo [3], catalyst contain  $\text{LaMn}_{0.9}\text{Pd}_{0.1}\text{O}_3$  deposited on cordierite monolith (supported by  $\gamma\text{-Al}_2\text{O}_3$ ) had almost the same  $T_{50}$  value as the commercial catalyst, but with a six-times lower noble metal load.

The aim of study was to establish a relation between catalytic activity in toluene oxidation and the amount of noble metal in different perovskites catalysts ( $\text{LaMnO}_3$  or  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$  as an active phase).

## Scope and methods

### Preparation of catalysts

Granular catalyst support, in a shape of balls (4 mm in diameter and density  $0.465 \text{ g/cm}^3$ ) were composed of Fe-Cr-Al steel. The catalyst balls were washcoated with an  $\gamma\text{-Al}_2\text{O}_3$ . The active phase,  $\text{LaMnO}_3$  or

$\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ , was placed by immersion washcoated balls in the prepared slurry, composed of adequate perovskite precursor (10 g), 5 g of Puralox ( $\text{Al}_2\text{O}_3$ ) with 50 ml distilled water. The catalysts prepared this way were dried at  $120^\circ\text{C}$  for 2 h, and calcined at  $600^\circ\text{C}$  for 4 h.

Catalysts doped with Pt or Pd were impregnated with the solution of platinum acetylacetonate, 98% Pt, Acros Organics, with acetone as the solvent or palladium acetate, 47% Pd, Merck, with toluene. After impregnation the catalysts were dried and calcined at the same conditions as earlier.

As a result, catalysts with 0.3, 0.75, 1.0, 1.5 wt% of Pt or Pd on  $\text{LaMnO}_3$  or  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$  was obtained.

### Methods of catalyst testing

The activity of catalysts prepared was tested in the oxidation of toluene. The tests were conducted in a glass flow reactor of 12 mm in diameter, electrically heated, with a programmed temperature, where 2 g of catalysts were placed. Concentration of oxidized compound reached  $5\text{ g/m}^3$ , the total gas flow velocity was  $14\text{ dm}^3/\text{h}$ . The tests were carried out during increase and decrease of the reaction temperature. The catalyst activity was measured by the concentration of oxidized compound at

the outlet of the reactor referred to the beginning concentration. VOCs concentration was measured with the gas chromatograph Agilent Technologies 6890N.

### Results

Figure 1 illustrates the toluene conversion (%) vs. temperature ( $^\circ\text{C}$ ) plots recorded for the catalysts considered.

In Fig. 1 (a), catalysts contain 0.3 wt% of noble metal, difference of activity of perovskite catalysts impregnated palladium solution can be observed. Temperature of 50% toluene conversion ( $T_{50}$ ) for  $\text{LaMnO}_3 + 0.3\%$  Pd catalyst reached  $186^\circ\text{C}$  and is  $30^\circ\text{C}$  lower than responding  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3 + 0.3\%$  Pd. Activity of catalysts containing platinum is almost equal,  $T_{50} = 130^\circ\text{C}$ .

In Fig. 1 (b), catalysts contain 0.75 wt% of noble metal, catalysts containing palladium showed similar activity  $T_{50} = 178^\circ\text{C}$ . The difference in activity of catalysts impregnated platinum solution was high. The most active catalytically was  $\text{LaMnO}_3 + 0.75\%$  Pt, temperature  $T_{50}$  amount to  $115^\circ\text{C}$ .  $T_{50}$  for  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3 + 0.75\%$  Pt catalyst was  $35^\circ\text{C}$  higher and reached  $150^\circ\text{C}$ .

It was observed that the higher level of concentrations of noble metal, Fig. 1 (c) and (d), type of applied perovskite is meaningless for catalytic activity. Once

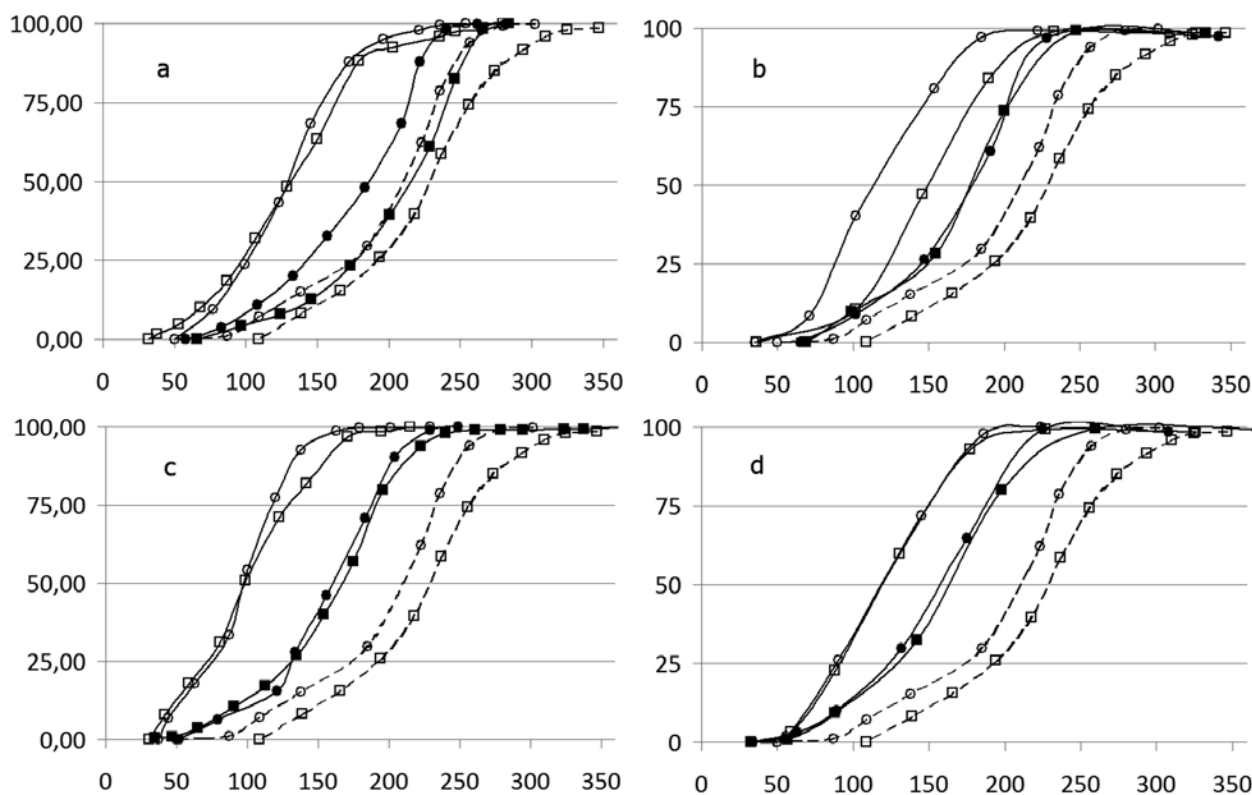


Fig. 1. Catalytic activity in toluene oxidation. Content of noble metal: (a) 0.3 wt%, (b) 0.75 wt%, (c) 1.0 wt%, (d) 1.5 wt%. Legend: -- ○ --  $\text{LaMnO}_3$ ; -- □ --  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ ; — ○ —  $\text{LaMnO}_3 + \text{Pt}$ ; — □ —  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3 + \text{Pt}$ ; — ● —  $\text{LaMnO}_3 + \text{Pd}$ ; — ■ —  $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3 + \text{Pd}$ .

Table 1. Temperatures of 50% and 90% toluene conversion for tested catalysts.

Content of noble metal	T <sub>50</sub> LaMnO <sub>3</sub>	T <sub>90</sub> LaMnO <sub>3</sub>	T <sub>50</sub> La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub>	T <sub>90</sub> La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub>
0.3% Pt	130	177	130	186
0.3% Pd	186	226	216	254
0.75% Pt	115	172	150	207
0.75% Pd	178	221	178	231
1.0% Pt	98	133	98	156
1.0% Pd	160	203	167	214
1.5% Pt	120	173	120	173
1.5% Pd	157	211	163	229

again higher activity is obtain over catalysts with Pt, however the most active catalytically phase in the oxidation of toluene among made were catalysts impregnated 1.0 wt% of Pt.

Temperatures of 50% and 90% toluene conversion are given in Table 1.

Furthermore, activation energy of conducted reactions assuming first-order model was computed (based on article Lei et al. 2010 [4]). The integrated expression of k is:

$$k = \frac{v_0}{W} \ln \frac{1}{1-x}$$

where:  $v_0$  — total volumetric flow rate of the gas phase at the inlet,  $\text{m}^3 \cdot \text{s}^{-1}$ ,

$W$  — catalyst mass, g,

$x$  — conversion of toluene, -.

According to the Arrhenius' Law, k is described by:

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

where: A — pre-exponential factor,

$E_a$  — activation energy.

An Arrhenius-type plot of  $\ln k$  versus  $1/T$  provides an estimate of  $E_a$  and A. Results are listed in Table 2.

Table 2. Activation energy of toluene oxidation, calculated for chosen catalysts.

Catalyst	$E_a$ [kJ/mol]
La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub>	43,3
La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub> +0.3%Pt	33,9
+0.75%Pt	39,4
+1.0%Pt	31,1
+1.5%Pt	32,2
La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub> +0.3%Pd	38,6
+0.75%Pd	41,7
+1.0%Pd	37,5
+1.5%Pd	37,3

The calculations show that toluene oxidation carried out on the catalysts contain 0.75 wt% of noble metal, had

the highest value of activation energy. On the other hand value of activation energy was the lowest when catalysts contain 1.0 wt% of Pt or Pd were used. It is responding to the results of catalytic activity, in which the most active were catalysts impregnated 1.0 wt% of platinum.

## Conclusions

Perovskites catalysts, impregnated solution of noble metal (platinum or palladium), show higher catalytic activity in toluene oxidation than not impregnated one.

Presented research revealed, that the catalysts contain LaMnO<sub>3</sub> had higher activity than catalysts with La<sub>0.75</sub>Ag<sub>0.25</sub>MnO<sub>3</sub>. However the way of preparation of catalysts may have crucial impact on the amount of perovskite coating it. The used method did not allow for equitable distribution of perovskite, so it is not possible to clearly determine which perovskite shows higher catalytic activity.

The activity catalysts impregnated platinum was greater than the corresponding activity of the catalysts with Pd, regardless of the applied perovskite.

According to the results of the research, the optimal composition of the catalyst applicable at the oxidation of toluene is LaMnO<sub>3</sub> + 1.0 wt% Pt.

## References

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