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EFFECT OF PLATINUM DOPING ON ACTIVITY OF LaMnO_3 IN OXIDATION OF VOLATILE ORGANIC COMPOUNDS

The activity of two monolithic catalysts, one based on LaMnO_3 alone and the other one on Pt-doped LaMnO_3 , was compared in the oxidation of hydrocarbons, oxygenated compounds and *n*-propylamine. In the oxidation of oxy-derivatives and amine, the LaMnO_3 catalyst showed a slightly lower, and in the oxidation of hydrocarbons a significantly lower activity as compared to the Pt-doped LaMnO_3 catalyst. Hydrocarbons were oxidized to CO_2 and water, the oxy-derivative compounds being oxidized via intermediates. Over the Pt-doped perovskite, deep oxidation of all the compounds tested took place practically above 320 °C, while in the presence of the LaMnO_3 perovskite, intermediate products were detected in the reaction gas even at the highest reaction temperatures.

1. INTRODUCTION

The ever rising prices of noble metals have directed the attention of scientists and engineers to the preparation highly active catalysts on the basis of metal oxides. Of these, perovskite structures have aroused particular interest. Perovskites display a catalytic activity which is particularly high in the oxidation of specific air pollutants (e.g. oxygenated compounds) but noticeably lower in the oxidation of hydrocarbons as compared to that of noble metals [1]–[3]. The addition of noble metals, i.e. platinum, palladium or gold, can visibly intensify the activity of the perovskite structure in the oxidation of all groups of pollutants [4], [5].

The aim of present study was to examine the effect of platinum doping on the activity of the LaMnO_3 perovskite in the oxidation of typical organic air pollutants differing in their chemical structure: hydrocarbons, oxy-derivatives and *n*-propylamine.

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2. METHODS

2.1. CATALYSTS CHARACTERISTICS

Two catalysts were chosen for the study; one based on the LaMnO_3 perovskite alone (PER), and the other one, on the Pt-doped LaMnO_3 perovskite (PER-Pt). Both were deposited onto a monolithic metal support prepared from a heat resisting steel foil of alumel type. The washcoat of the PER catalyst consisted of $\gamma\text{-Al}_2\text{O}_3$ (with the addition of TiO_2 and La_2O_3) in the total amount of 2 wt.%. The perovskite precursor was obtained from the water solutions of lanthanum nitrate and manganese nitrate. The active ingredient was deposited by immersion of the washcoated support in the suspension of the perovskite precursor in citric acid, followed by its drying and calcination at 500 °C for 3 h. The washcoat of the PER-Pt catalyst consisted of $\gamma\text{-Al}_2\text{O}_3$ (with the addition of 5 wt.% SiO_2), and was deposited in the amount of 2.15 wt.%. The support prepared via the above route was immersed in the water suspension of the LaMnO_3 perovskite precursor and $\gamma\text{-Al}_2\text{O}_3$ (impregnated with platinum in the amount of 0.5 wt.%), in 1:2 proportion. The catalyst prepared was dried for 1 h at 200 °C and calcined for 5 h at 600 °C. The content of the active ingredient in both catalysts amounted to ca. 20 wt.%. For both catalysts the length of the side of the triangular cell, the number of cells, and the open surface area amounted to approx. 0.9 mm, 112/cm², and 84%, respectively.

2.2. TESTING METHODS

The catalysts were placed in a glass reactor electrically heated. The temperature of the reaction was controlled and recorded with a thermoelement placed inside the catalyst block. The vapours of the compounds tested were produced in a special doser and mixed with air to the concentration desired (approximately 1 g/m³). Oxidation tests were conducted within the reaction temperature range of 200–500 °C at a constant space velocity of 10,000 h⁻¹.

The activity of the catalysts was tested in the oxidation of the hydrocarbons (toluene and *n*-hexane), oxygenated compounds (ethanol, acetone and ethyl acetate), and *n*-propylamine. Qualitative and quantitative analyses of the compounds tested and of the potential organic reaction intermediates were performed by gas chromatography using an N-504 Mera Elwro chromatograph, with a flame ionization detector and packed columns, coupled to a computer. Amine concentration was analyzed in a column packed with a 60/80 Carbowax B 4% Carbowax R 20M (0.8% KOH), at a temperature of 180 °C. The other compounds were analyzed in a column packed with 10% DC-200 Gas-Chrom Q 100–120 mesh, at a temperature of 120 °C. The temperature of the injector and detector was 200 °C. Additionally, the concentrations of nitrogen oxides and carbon oxide were measured during amine oxidation using a PG-250

Horiba gas analyzer; the read off concentration values, expressed in ppm, were converted into g/m³.

3. RESULTS

The results of activity tests obtained over the two catalysts examined are plotted in figures 1 and 2, and compiled in table. Besides the conversion of the oxidized compounds, the plots show the concentrations of the organic reaction products yielded and additionally the concentration of CO, NO and NO₂ produced during oxidation of *n*-propylamine. The catalyst activity was determined taking into account the conversion of the compounds tested, calculated from their concentrations at the inlet and outlet of the reactor.

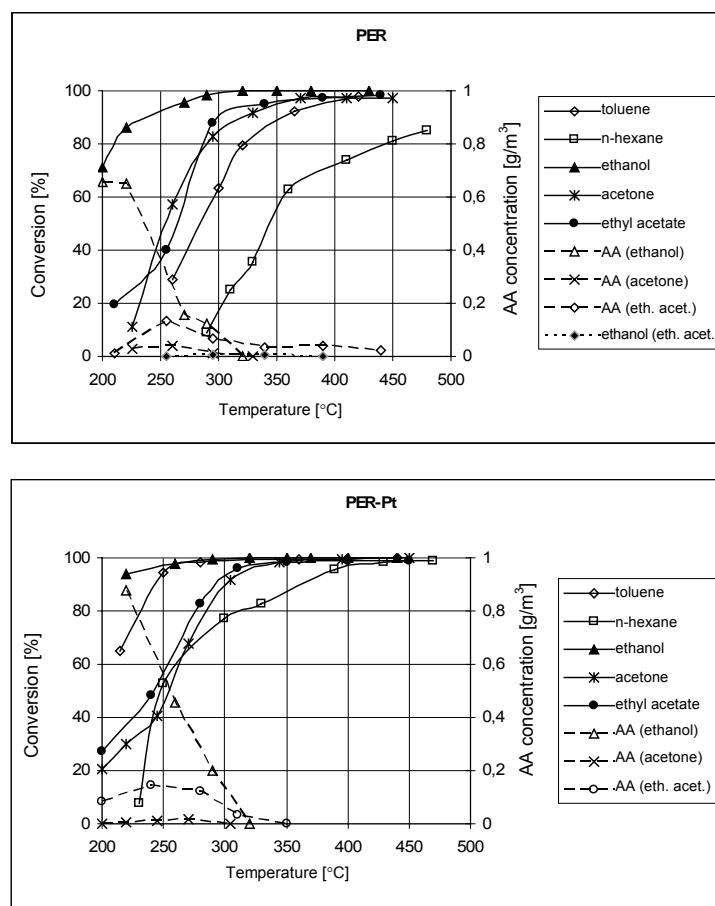


Fig. 1. Results of hydrocarbon and oxy-derivative conversion and concentrations of reaction intermediates yielded

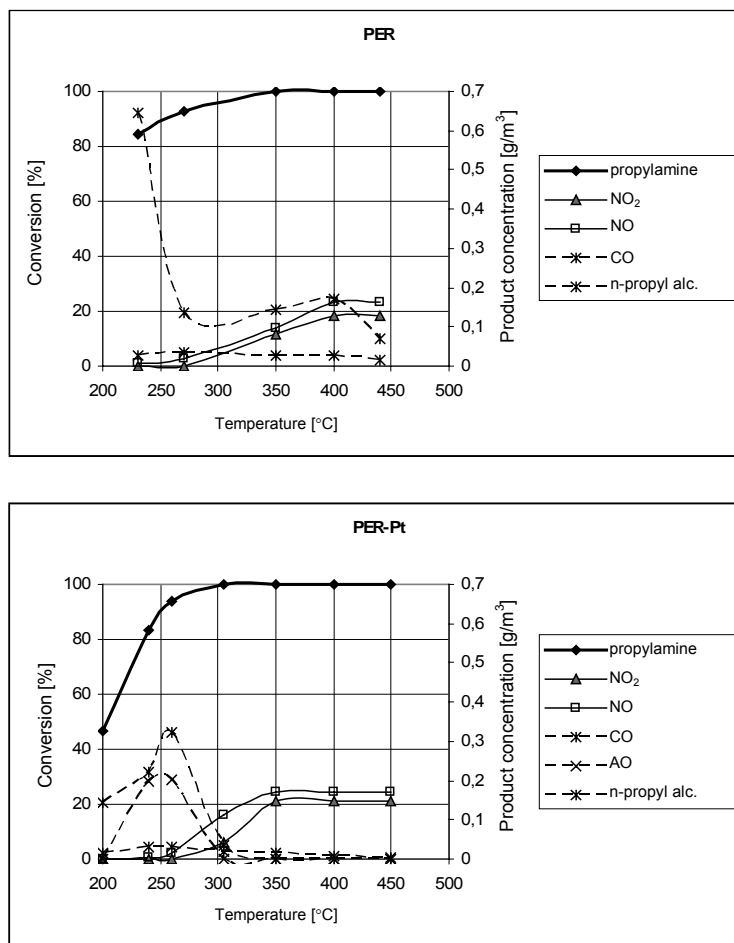


Fig. 2. Results of *n*-propylamine conversion and reaction product concentrations

The results of oxidizing both hydrocarbons and oxy-derivatives are shown in figure 1. The oxidation of *n*-propylamine is shown in figure 2. The table compares the temperature of 50% and 95% conversion of the compounds tested, obtained over the two catalysts.

Over the PER catalyst, the reactivity of the compounds being oxidized decreased in the following order: ethanol > *n*-propylamine > ethyl acetate = acetone > toluene > *n*-hexane; in the presence of PER-Pt this order was as follows: ethanol > toluene > *n*-propylamine > ethyl acetate = acetone > *n*-hexane. In both instances, ethanol was most readily oxidized, and a 95% conversion was achieved at 225 °C and 270 °C over PER-Pt and PER, respectively. Of the compounds tested, *n*-hexane was the most resistant to oxidation. In the presence of PER-Pt, its 95% conversion was attained at

385 °C, while over PER the conversion of *n*-hexane amounted solely to 85% at the highest reaction temperature applied (480 °C). A similar conversion pattern over the two catalysts was observed with *n*-propylamine, acetone and ethyl acetate. Thus, 95% conversion of amine was achieved within the temperature range of 270–280 °C, and the same conversion of ethyl acetate and acetone at 350 °C and 320 °C, in the presence of PER and PER-Pt, respectively. The beneficial effect of platinum was particularly distinct in the oxidation of toluene, which should be attributed to the fact that platinum is a particularly efficient catalyst in the oxidation of aromatic hydrocarbons [6]. In the presence of the LaMnO₃ catalyst, 95% conversion of toluene was achieved at 390 °C, and the addition of platinum caused this temperature to decrease to 250 °C.

Table

Temperatures (°C) of 50% and 95% (T_{50} , T_{95}) conversion of compounds tested

Compound	PER		PER-Pt	
	T_{50}	T_{95}	T_{50}	T_{95}
Toluene	280	390	200	250
<i>n</i> -Hexane	340	> 480	245	385
Etanol	< 200	270	< 200	225
Acetone	255	350	255	320
Ethyl acetale	270	350	240	320
<i>n</i> -Propylamine	< 225	280	205	260

3.1. ANALYSIS OF REACTION PRODUCTS

Both hydrocarbons tested were oxidized to CO₂ and water and no organic reaction intermediates were found during their oxidation. All of the oxy-derivative compounds tested were oxidized via acetaldehyde (AA), a typical product of incomplete combustion. Thus, over PER and PER-Pt, the highest AA concentrations, 0.66 and 0.9 g/m³, respectively, were detected during ethanol oxidation within the lowest range of the reaction temperatures, i.e. 200–220 °C. However, regardless of which of the two catalysts was applied, no aldehyde was detected at temperatures higher than 320 °C. Significantly lower AA concentrations were measured in the course of acetate oxidation. The highest values, amounted to 0.13 and 0.14 g/m³ only, were detected at 250 °C over PER and PER-Pt, respectively. In the presence of PER-Pt, aldehyde was absent at temperatures exceeding 350 °C. Over the LaMnO₃ perovskite catalyst, AA was detected even at the highest temperature applied, i.e. of 440 °C, at an almost complete conversion of acetate. Besides AA, the reaction gases contained ethanol, a product of partial acetate hydrolysis [6], when use was made of the PER catalyst. It is essential to note, however, that these were in trace amounts only. Ethanol was not detected when acetate was oxidized over the Pt-doped perovskite. The lowest AA

concentrations were measured during acetone oxidation – they did not exceed 0.04 and 0.017 g/m³ in the presence of PER and PER-Pt, respectively.

As for the reaction by-products of *n*-propylamine oxidation, *n*-propyl alcohol was found in the highest concentrations. In the presence of PER, the highest concentration of the alcohol, 0.65 g/m³, was determined at 230 °C, but this intermediate product was practically detected within the entire range of the temperatures applied. In the presence of PER-Pt, *n*-propyl alcohol was measured below 350 °C, but its highest concentration determined at 260 °C amounted to 0.32 g/m³ only. Over the same catalyst, also AA was detected at temperatures below 305 °C; the highest concentration, which equalled 0.25 g/m³, being measured at 255 °C. The concentrations of the other compounds analyzed, i.e. CO, NO and NO₂, were similar for the two catalysts, although the concentrations of CO above 400 °C were visibly lower for PER-Pt. In the presence of the Pt-doped perovskite catalyst, the concentrations of the two nitrogen oxides showed similar values at temperatures higher than 350 °C and did not undergo changes. At lower reaction temperatures the NO_x concentrations were slightly lower for the PER catalyst than for the PER-Pt one. This is to be attributed to the slightly lower activity of the catalyst solely based on metal oxides for the oxidation of the nitrogen in the amine molecule to NO and NO₂. Our previous investigations into the oxidation of aliphatic amines have substantiated the high activity of the catalyst based on Cu-Cr-Mn oxides, and simultaneously a very low concentration of the nitrogen oxides being formed [8].

4. SUMMARY

The monolithic LaMnO₃ perovskite catalyst showed a high activity in the oxidation of *n*-propylamine and oxygenated compounds, which is comparable to that of the Pt-doped LaMnO₃ catalyst. During amine oxidation, however, large quantities of NO_x were formed in the course of the process over either of the two catalysts examined, and this practically eliminates their application to such uses. On the other hand, the LaMnO₃-based catalyst showed a noticeably lower activity in the oxidation of both hydrocarbons – toluene and *n*-hexane. The addition of platinum significantly enhanced the activity of the perovskite in the oxidation of hydrocarbons.

The hydrocarbons tested were oxidized to CO₂ and water. During oxidation of oxy-derivative compounds, acetaldehyde, a typical product of incomplete combustion, was detected in the reaction gases. The highest concentration of AA was measured in the process of ethanol oxidation, and this concentration was significantly lower when ethyl acetate or acetone were combusted. During *n*-propylamine oxidation, the reaction gases contained acetaldehyde, *n*-propyl alcohol and carbon oxide. The concentrations of NO and NO₂ produced were similar for both catalysts and were relatively high.

In every instance when the oxidation reaction was conducted in the presence of the Pt-doped perovskite catalyst, practically no intermediates were detected at temperatures higher than 320 °C, while over the LaMnO_3 -based catalyst intermediate products were present even at the highest reaction temperatures applied.

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WPLYW DODATKU PLATYNY NA AKTYWNOŚĆ LaMnO_3
W UTLENIANIU LOTNYCH ZWIĄZKÓW ORGANICZNYCH

Porównano aktywność utleniania wybranych związków, tzn. węglowodorów, połączeń tlenowych i *n*-propyloaminy, w obecności dwóch katalizatorów monolitycznych na bazie perowskitu LaMnO_3 , samego i z dodatkiem platyny. W utlenianiu pochodnych tlenowych i aminy sam LaMnO_3 wykazał nieznacznie niższą aktywność niż perowskit domieszkowany platyną, jednak znacząco niższą w utlenianiu obu węglowodorów. Węglowodory spalały się do CO_2 i wody, pozostałe związki poprzez produkty pośrednie. Perowskit z dodatkiem platyny umożliwił głębokie utlenianie wszystkich testowanych związków praktycznie powyżej 320 °C, podczas gdy w obecności samego perowskitu produkty pośrednie w gazach preakcyjnych wykrywano nawet w najwyższych testowanych temperaturach (do 470 °C).