

## OXIDATION OF CARBON MONOXIDE BY OXYGEN OVER PURE AND PLATINUM-DOPED $\text{LaMnO}_3$ PEROVSKITES

Jaroslav BARTOŇ and Vladimír POUR

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 160 00 Prague 6*

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The properties of pure and platinum-doped  $\text{LaMnO}_3$  perovskites, including their catalytic activities for the reaction of CO with oxygen, have been determined. Perovskite samples were prepared by decomposition of lanthanum and manganese citrates. The surface areas were  $12.2 \text{ m}^2/\text{g}$  for pure  $\text{LaMnO}_3$  and  $9.8 \text{ m}^2/\text{g}$  for the platinum-doped sample. The doping with a small amount of platinum markedly enhances the catalytic activity of  $\text{LaMnO}_3$  perovskite. The ( $\text{CO} + \text{O}_2$ ) reaction starts at  $200^\circ\text{C}$  over  $\text{LaMnO}_3$  and at temperatures below  $100^\circ\text{C}$  over a sample doped with Pt. The reaction kinetics for both the pure and platinum-doped  $\text{LaMnO}_3$  can be described by empirical equation (4). When Pt-doped perovskite is used, an increase in the apparent activation energy occurs at about  $150^\circ\text{C}$ . This fact is attributed to a change in the mechanism of CO oxidation.

Double oxides of the general formula  $\text{ABO}_3$ , where A represents a rare-earth element and B represents a cation usually from the group of transition metals, also called perovskites according to the character of their crystal structure, continue to be in the foreground of interest not only as electrode materials<sup>1</sup> or materials with superconducting properties<sup>2,3</sup>, but also because of their good catalytic properties<sup>4-13</sup> and satisfactory thermal stability<sup>7</sup>. Perovskites of the type  $\text{LaCoO}_3$ <sup>4,5,11</sup> and  $\text{LaMnO}_3$ <sup>6-8</sup> have proved very useful. Combination of various cations as well as doping, especially by rare metals, make it possible to obtain materials with diverse physical, chemical and catalytic properties suitable for a wide range of catalytic processes. A particularly important process is the catalytic oxidation of carbon monoxide, both as a way to remove CO from various waste gases discharged from chemical and other processes and as part of exhaust gas detoxication. In the present work, we have studied the oxidation of CO by oxygen catalyzed by  $\text{LaMnO}_3$  and the same catalyst doped with platinum, of the empirical formula  $\text{LaMn}_{1-x}\text{Pt}_x\text{O}_3$ , where  $x = 0.01$ .

### EXPERIMENTAL

A sample of  $\text{LaMnO}_3$  was prepared by the method described by Tascón and co-workers<sup>11</sup>. A concentrated solution of citric acid was added to a concentrated solution of the appropriate amounts of lanthanum(III) and manganese(II) nitrates. The product was evaporated with constant

stirring until it attained a syrupy consistency, and then dried in a vacuum oven at  $100^\circ\text{C}$ . The resulting amorphous product was heat treated in a stream of air at  $600^\circ\text{C}$  for 8 h. The temperature and time of calcination had been determined by preliminary measurements and ensured the formation of the perovskite structure while maintaining a large surface area of the sample.

Platinum-doped perovskite was prepared in the same way except that the concentrated solution of nitrates was mixed with an amount of hexachloroplatinic(IV) acid such that the proportion of Pt in the perovskite corresponded to 1 mole % of manganese. In this case, the optimum temperature and time of calcination were found to be  $700^\circ\text{C}$  and 8 h, respectively.

The structure of the samples was determined by X-ray measurements using a DRON 1 instrument.

The valence state of platinum in the doped sample was determined from photoemission spectra measured on an ESCA III Mk II instrument.

The perovskites were further characterized by the specific surface area and electrical conductivity. The specific surface area was determined by means of nitrogen adsorption from a nitrogen-hydrogen mixture in a chromatographic arrangement. The adsorbed amount was determined catharometrically from the change in thermal conductivity. The surface area was calculated from the BET equation. The electrical conductivity was determined by the four-point method described by Van der Pauw<sup>14</sup>.

The activity and reaction kinetics were determined using an all-glass apparatus with an integral plug flow reactor made of quartz. The catalyst of 0.8–1 mm grain size, determined experimentally with elimination of diffusion effects, was mixed with quartz cullet of the same grain size in a volume ratio of 1 : 10. The temperature in the catalyst bed was measured with a Fe-Co thermocouple placed on the axis at the centre of the layer. The catalyst weight was 1 g. The determination was made at  $W/F$  values (where  $W$  is the catalyst mass and  $F$  is the flow rate of the gaseous mixture at the reactor inlet) of 2 to  $8 \text{ g h mol}^{-1}$ . The inlet reaction mixtures with  $\text{CO} : \text{O}_2$  molar ratios of 1 : 0.5, 1 : 1 and 1 : 1.5 contained 4% of the reagents in Ar. The measurements were performed in the temperature range  $200\text{--}400^\circ\text{C}$  for  $\text{LaMnO}_3$  and at  $100\text{--}300^\circ\text{C}$  for the platinum-doped perovskite. The amounts of  $\text{CO}_2$  and unreacted CO were determined chromatographically. The oxygen consumption was calculated from balance equations.

## RESULTS AND DISCUSSION

*Characterization of catalysts.* The perovskite structure was characterized by lines in the X-ray diffraction pattern and the corresponding  $d$ -values to which the corresponding  $h$ ,  $k$  and  $l$  indices were assigned. The calculated lattice constant,  $a = 0.3897 \text{ nm}$ , is in good agreement with the tabulated value<sup>15</sup> for  $\text{LaMnO}_3$  perovskite, i.e.  $0.3896 \text{ nm}$ . The remaining lines were assigned, by comparison with tabulated data<sup>16</sup>, to  $\text{La}_2\text{O}_3$  with a hexagonal crystal lattice. The calculated lattice constant for platinum-doped perovskite,  $a = 0.3848$ , is also in good agreement with the tabulated value<sup>15</sup>. In this case, the  $d$ -values not corresponding to perovskite structure were attributed to the crystal lattice of platinum. The obtained average value of the lattice constant of platinum,  $0.3931 \text{ nm}$ , is also in good agreement with the tabulated value<sup>15</sup>,  $0.39236 \text{ nm}$ .

The above given values confirm the presence of perovskite structure in both samples. The lattice constant for platinum-doped perovskite is somewhat lower than

that for pure  $\text{LaMnO}_3$ . The difference may be due to the  $\text{Pt}^{4+}$  ion which apparently replaces part of manganese in the perovskite. This replacement is possible because the radii of the two ions are very close,  $r(\text{Pt}^{4+}) = 0.064 \text{ nm}$  and  $r(\text{Mn}^{3+}) = 0.065 \text{ nm}$ , and the inequality derived by Goodenough<sup>12</sup> is fulfilled.

The photoemission spectrum obtained by the ESCA method and the separated bands shown in Fig. 1 indicate that the perovskite contains platinum in two forms, as the  $\text{Pt}^{4+}$  ion and in the metal state. The results are comparable with data of Johnson and co-workers<sup>6</sup>, who have measured the ESCA spectrum of platinum-doped  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  perovskite and arrived at similar conclusions. A summary of characteristic properties of the prepared perovskite samples is given in Table I.

TABLE I  
Characteristics of perovskite samples

Sample	Surface area $\text{m}^2/\text{g}$	Electric conductivity $\cdot 10^{-5} \Omega^{-1} \text{ cm}$	Structure	Admixture
$\text{LaMnO}_3$	13.3	1.9	Perovskite $a = 0.3898 \text{ nm}$	$\text{La}_2\text{O}_3$
$\text{LaMnO}_3(\text{Pt})$	9.8	2.3	Perovskite $a = 0.3848 \text{ nm}$	$\text{Pt}^0, \text{Pt}^{4+}$

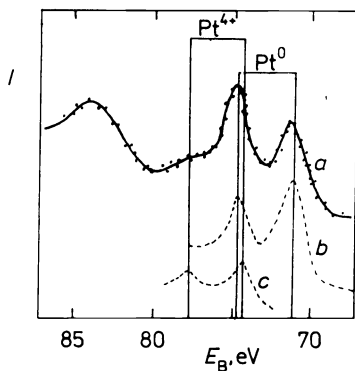


FIG. 1

Photoemission (ESCA) spectrum of platinum-doped  $\text{LaMnO}_3$  perovskite: *a* measured photoemission spectrum; *b*, *c* separated bands

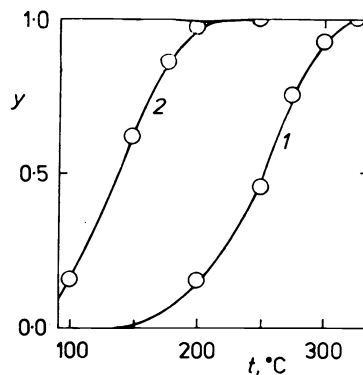


FIG. 2

Variation in CO conversion with temperature. Catalyst: 1 pure  $\text{LaMnO}_3$ ; 2 platinum-doped  $\text{LaMnO}_3$

*Kinetics of the reaction of CO with oxygen.* As indicated by plots of the degree of CO conversion against the temperature at a constant concentration, an inlet CO : O<sub>2</sub> ratio of 1 : 1, and  $W/F = 4 \text{ g h mol}^{-1}$  (see Fig. 2), both catalysts show very good activity for the reaction. In the case of LaMnO<sub>3</sub>, the reaction starts at temperatures around 170°C and 100% conversion is attained at about 300°C. When the platinum-doped perovskite is used, the start of the reaction is observed already at temperatures below 100°C, and 100% conversion is approached at about 200°C.

In order to better evaluate and compare the catalysts, we used a method described in our previous paper<sup>17</sup> to calculate the reaction rates from measured kinetic isotherms (dependences of CO conversion on  $W/F$ ). These were first fitted by nonlinear regression to the empirical function

$$y = 1 - \left[ \sum_{i=0}^{n+1} A_i (W/F)^i \right] \exp(BW/F), \quad (1)$$

where  $y$  is the overall conversion of CO, and  $n$  is the polynomial degree. The parameters  $A_i$  and  $B$  were estimated on the assumption that  $A_0 = 1$  and  $B < 0$ , where Eq. (1) gives generally a good fit of the kinetic isotherms.

The relationship for the reaction rate,  $r = c_0 dy/d(W/F)$ , where  $c_0$  is the inlet concentration of CO, was then adapted by inserting the derivative of Eq. (1) to give

$$r = -c_0 \exp[B(W/F)] \sum_{i=0}^{n+1} A_i (W/F)^{i-1} (i + BW/F). \quad (2)$$

So obtained reaction rates were then fitted to an empirical relationship of the form

$$r = k p_{\text{CO}}^a p_{\text{O}_2}^b p_{\text{CO}_2}^c, \quad (3)$$

where  $p_{\text{CO}}$ ,  $p_{\text{O}_2}$  and  $p_{\text{CO}_2}$  are the partial pressures of the individual reaction components, and  $a$ ,  $b$ ,  $c$  and  $k$  are adjustable parameters, with  $k$  representing the rate constant. Using methods of quasilinear and nonlinear regression to adjust the parameters and expressing the adjusted exponents as geometrical averages over all the temperatures, we obtained the following empirical relationship

$$r = k p_{\text{CO}} p_{\text{O}_2}^{0.4} p_{\text{CO}_2}^{-0.5}. \quad (4)$$

Values of the rate constant  $k$  and the most important statistical parameters for various temperatures are given in Tables II and III. The statistical parameters indicate that the above equation gives a good representation of the reaction kinetics over the measured range, with the average relative error never exceeding 9%. The estimated correlation coefficients of the parameters, which are all close to zero, indicate that the reaction rate is independent of the individual reaction components. The constant

TABLE II  
Rate constants  $k$  of Eq. (4) at various temperatures for the (CO + O<sub>2</sub>) reaction over LaMnO<sub>3</sub>

$t$ °C	$k$ mol h <sup>-1</sup> g <sup>-1</sup> . MPa <sup>-0.9</sup>	Estimate of dispersion in $k \cdot 10^4$	Average relative error $r$ , %	Standard deviation $\sigma \cdot 10^3$
200	0.2735	9.61	8.3	3.65
250	0.4900	4.34	3.2	2.68
275	0.7487	0.63	0.9	1.2
300	0.9547	0.65	1.7	1.5

TABLE III  
Rate constants  $k$  of Eq. (4) for the (CO + O<sub>2</sub>) reaction over platinum-doped LaMnO<sub>3</sub> at various temperatures

$t$ °C	$k$ mol h <sup>-1</sup> g <sup>-1</sup> . MPa <sup>-0.9</sup>	Estimate of dispersion in $k \cdot 10^4$	Average relative error $r$ , %	Standard deviation $\sigma \cdot 10^3$
100	0.2748	5.46	8.9	4.33
125	0.3229	0.39	2.7	4.04
150	0.3987	0.78	3.3	3.43
175	0.6292	0.95	1.4	1.38
200	0.8946	1.92	0.6	0.93

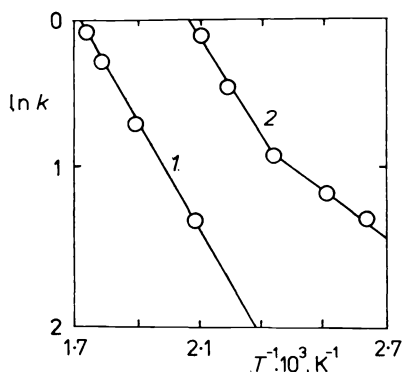


FIG. 3  
Arrhenius dependence of the rate constant of kinetic equation (4). Catalyst: 1 pure LaMnO<sub>3</sub>; 2 platinum-doped LaMnO<sub>3</sub>

k depends on the temperature only. The Arrhenius dependences of the rate constant for the reaction over pure and platinum-doped LaMnO<sub>3</sub> perovskites are represented in Fig. 3.

The plot for the platinum-doped LaMnO<sub>3</sub> perovskite shows a distinct break at about 150°C. The apparent activation energy is 10.5 kJ/mol in the temperature range below 150°C and 27.9 kJ/mol above 150°C. Low values of the apparent activation energy and nonlinear Arrhenius dependence of the rate constant for the reaction of CO with oxygen have also been observed by other investigators<sup>18-21</sup> for various catalysts. In accord with these investigators, we may conclude that the change in the activation energy is due to a change in the reaction mechanism. It is assumed that the low-temperature oxidation characterized by the low activation energy occurs by an adsorption mechanism, while an oxidation-reduction mechanism operates at higher temperatures.

With pure LaMnO<sub>3</sub> perovskite, the reaction occurred at temperatures much above that at which the break in the Arrhenius plot was observed. In the temperature range of measurement, whose lower limit of 200°C is given by the catalytic activity of the LaMnO<sub>3</sub> perovskite, the oxidation of CO by oxygen proceeds apparently without any change, the activation energy being 32.23 kJ/mol.

From the values of the exponents of empirical equation (4) it may be concluded that gas-phase or only weakly adsorbed carbon monoxide is involved in the reaction; oxygen is preferentially adsorbed on the catalyst surface, and the CO<sub>2</sub> product inhibits the oxidation.

Comparison of the data for the kinetics of CO oxidation by oxygen over the two perovskite samples indicates that the doping of LaMnO<sub>3</sub> with a small amount of platinum facilitates the reaction at relatively low temperatures by lowering the activation energy. So prepared catalytic material could be used not only for detoxication of exhaust gases, but also in special cases such as flameless combustion of CO.

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