
**REDUCTION OF NITROGEN OXIDE BY CARBON MONOXIDE OVER
PURE AND PLATINUM-DOPED LaMnO_3 PEROVSKITES.
EFFECT OF OXYGEN ON THE REACTION**

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The reduction of NO by CO has been studied using pure and platinum-doped LaMnO_3 perovskites as catalysts. The reaction products always include nitrogen monoxide, whose amount varies with temperature. The reaction kinetics for the two catalysts are different and have been described by different rate laws. Considerable differences have also been found in the apparent activation energies: in the presence of Pt it is about half that for the reaction catalyzed by pure LaMnO_3 . Both the catalysts exhibit good catalytic properties, but the platinum-doped LaMnO_3 shows a higher catalytic activity. The presence of oxygen in the inlet mixture affects considerably the kinetics of the reaction catalyzed by platinum-doped LaMnO_3 . The conversion of NO passes through a maximum at an oxygen/carbon monoxide molar ratio, m , of 1.8. At $m > 1.8$, CO is oxidized preferentially by oxygen rather than by NO.

The catalytic reduction of nitrogen oxide by carbon monoxide is an important chemical process because of the need to control NO and CO emissions, especially from motor vehicles. This process is advantageous since both the components are removed, leaving carbon dioxide and nitrogen.

Since nitrogen monoxide is almost always found among the reaction products, it is assumed that the reaction proceeds essentially in two steps:



A number of catalysts, based on rare metals^{1,2,7}, alloys³ and oxides^{1,4-6}, have been proposed for the process. It has been shown that oxides with perovskite structure exhibit good catalytic properties as well as the required thermal stability¹. The most extensively studied of these catalysts are perovskites containing a rare-earth element, especially lanthanum, and a transition metal, especially cobalt^{1,8-10} and manganese^{1,8-13}.

The reduction of nitrogen oxide by carbon monoxide has been classified by Voorhoeve and co-workers¹ as an intrafacial process involving oxygen of the perovskite lattice. In this case, the valence state of the catalyst changes rapidly depending on the gas-phase composition. Sorenson and co-workers⁹ have reported that the reduction rate is proportional to the degree of imperfection in stoichiometry, i.e. to the occurrence of anion (oxygen) vacancies. Voorhoeve and co-workers¹ have arrived at the conclusion that the reduction of NO on Mn perovskites proceeds via N_2O as an intermediate. Other intermediates observed in the reaction over perovskites were isocyanates¹⁴ and in some cases urea¹⁵.

The aim of the present work was to determine the kinetics of the reaction between nitrogen oxide and carbon monoxide over pure and platinum-doped $LaMnO_3$ perovskites and the effect of oxygen on the reaction. This paper is a continuation of a previous study¹⁶ on the oxidation of CO by oxygen over the same catalysts.

EXPERIMENTAL

Pure and platinum-doped $LaMnO_3$ perovskites were prepared in the same way as described earlier¹⁶. The platinum content of the doped perovskite corresponded to the stoichiometry $LaMn_{0.99}Pt_{0.01}O_3$.

The reaction was carried out in an all-glass apparatus with an integral plug flow reactor, using 1 g of catalyst having 0.8–1 mm grain size. The temperature range of measurement was chosen as 300–500°C for pure $LaMnO_3$ and as 200–400°C for the platinum-doped catalyst. The quantity W/F , where W is the catalyst mass (g) and F is the flow rate of inlet gas mixture ($mol\ h^{-1}$), was 2–8 $g\ h\ mol^{-1}$ for both catalysts. The inlet reaction mixtures with NO : CO molar ratios of 1 : 1 and 1 : 2 contained 4% of the reagents in Ar. The reaction mixtures at the inlet and outlet were analyzed chromatographically¹⁷.

RESULTS AND DISCUSSION

As shown by the plot of NO conversion against temperature in Fig. 1, both the pure and platinum-doped $LaMnO_3$ perovskites exhibit good catalytic properties for the reduction of NO by carbon monoxide. With pure $LaMnO_3$, the reaction starts at about 250°C, and 100% conversion of NO is reached at 500–550°C. With the platinum-doped perovskite, the reaction is observed already at 200°C and full conversion is attained at 400°C. Comparison of these data obtained under the same conditions, i.e. the same inlet concentration of reagents, a NO : CO molar ratio of 1 : 1, and $W/F = 4\ g\ h\ mol^{-1}$, indicates that platinum-doped perovskite possesses a higher catalytic activity than pure $LaMnO_3$.

The reaction products obtained in the measured temperature and concentration ranges always included nitrogen monoxide. As seen in Figs 2 and 3, the concentration of N_2O goes through maxima at 450°C for pure $LaMnO_3$ and at 320°C for platinum-doped perovskite. Thus it may be concluded that the reduction of NO by carbon

monoxide over the catalysts employed proceeds via N_2O as an intermediate, and the conjecture of Voorhoeve and co-workers¹ may be extended to platinum-doped LaMnO_3 . Nitrogen monoxide may be generated as an intermediate of consecutive reactions, but may also be formed in parallel reactions.

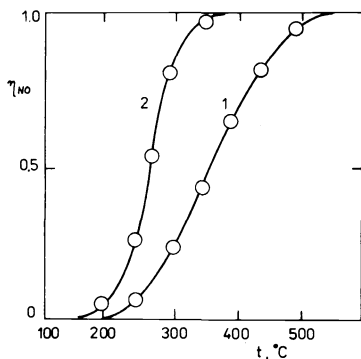


FIG. 1
Variation in NO conversion with temperature. Catalyst: 1 LaMnO_3 ; 2 $\text{LaMn}_{0.99}\text{Pt}_{0.01}\text{O}_3$

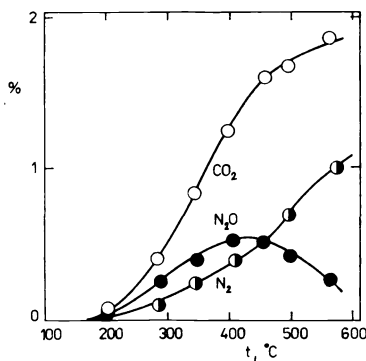


FIG. 2
Variation in the concentration of products from NO reduction by CO over LaMnO_3 with temperature at $W/F = 4 \text{ g h mol}^{-1}$

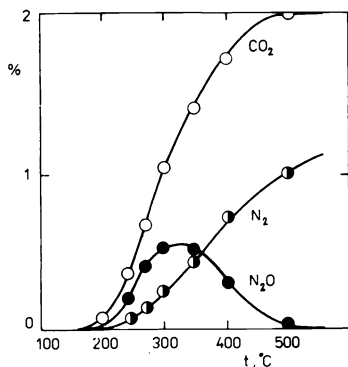


FIG. 3
Variation in the concentration of products from NO reduction by CO over $\text{LaMn}_{0.99}\text{Pt}_{0.01}\text{O}_3$ with temperature at $W/F = 4 \text{ g h mol}^{-1}$

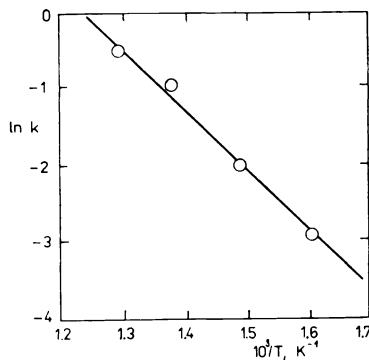


FIG. 4
Arrhenius dependence of the rate constant k_1 of Eq. (1) for LaMnO_3

In order that the catalytic properties of the two perovskites be compared more exactly, measured kinetic isotherms were used to evaluate the reaction rates as a function of the gas-phase composition in the same way as previously¹⁶. An empirical equation of the type $r = k p_{\text{NO}}^a p_{\text{CO}}^b p_{\text{N}_2\text{O}}^c p_{\text{CO}_2}^d p_{\text{N}_2}^e$, where r is the reaction rate, k is the rate constant, and p_i is the partial pressure of component i , was chosen to describe the reaction kinetics, and the parameters of this equation were estimated by weighted quasilinear and nonlinear regression methods. The exponents at the partial pressures of N_2 and N_2O approach zero for both catalysts, and thus the reaction rate only depends on the concentrations of the inlet components NO and CO and of the CO_2 product. The resulting rate law for the reaction of NO with CO over pure LaMnO_3 is

$$r = k_1 p_{\text{NO}} p_{\text{CO}}^{0.1} p_{\text{CO}_2}^{-0.73} \quad (1)$$

Estimates of the rate constant k_1 and some statistical parameters are listed in Table I. The apparent activation energy derived from the Arrhenius dependence of the rate constant k_1 (see Fig. 4) is equal to 64 kJ/mol.

The same procedure was used for the reaction catalyzed by platinum-doped LaMnO_3 perovskite. In this case, however, the correlation coefficient v_{c-k} for the estimate of the exponent at p_{CO_2} (-0.989) was found to be 0.43, indicating that the condition of the independence of the parameters c and k , and hence the independence of the term $p_{\text{CO}_2}^c$ on the rate constant k_1 , was not fulfilled. Thus the chosen form of the power law did not satisfy the basic requirement of mutual independence of the terms of the equation.

On the basis of the experience that a rational function may provide a good description of reaction kinetics, the kinetic term $1/(1 + a p_{\text{CO}_2})$ was used instead of $p_{\text{CO}_2}^c$.

TABLE I
Rate constants k_1 of Eq. (1) for the reduction of NO by CO over pure LaMnO_3 at various temperatures

t °C	k_1 $\text{mol h}^{-1} \text{g}^{-1} \cdot \text{MPa}^{-0.37}$	Estimate of dispersion, $k_1 \cdot 10^5$	Average relative error, r , %	Standard deviation $\cdot 10^3$
300	0.0280	2.8	2.7	2.3
350	0.0565	11.4	7.1	4.1
400	0.1280	9.3	2.7	2.0
450	0.4092	3.1	4.0	3.6
500	0.6065	4.7	6.2	3.7

Evaluation of the parameters by a nonlinear regression method resulted in the empirical equation

$$r = k_2 p_{\text{NO}} p_{\text{CO}}^{0.073} / (1 + a p_{\text{CO}_2}), \quad (2)$$

where a is an adjustable parameter with the dimension of reciprocal pressure. This rate law gives a very good description of the reaction kinetics for $a = 1 \pm 0.05 \text{ kPa}^{-1}$. The values of the rate constant k_2 for $a = 1$ and some statistical parameters are listed in Table II. The apparent activation energy for the reaction catalyzed by platinum-doped LaMnO₃ has been estimated to be 36 kJ/mol.

A plot of $\ln k_2$ against $1/T$ (see Fig. 5) is not exactly linear and shows a distinct break at about 300°C. In the same region, the highest N₂O content was measured in the reaction products. This suggests that, as the temperature is increased, reactions producing N₂O operate to an increasing extent until dramatic changes occur in the reaction course, resulting in nonlinearity of the temperature dependence of the rate constant. The break in the Arrhenius dependence is an indication of a lower apparent activation energy at higher temperatures. From this observation it may be concluded that the process may involve various parallel reactions, of which at least one results in the formation of N₂O.

Comparison of rate laws (1) and (2) shows that the reaction kinetics for the two catalysts are not entirely identical, even though they have some common features. In both cases, the exponent at p_{NO} is equal to 1, indicating that gas-phase or only weakly adsorbed NO is involved in the reaction. The exponent at p_{CO} is very small for both catalysts, and the negative exponent at p_{CO_2} indicates that CO₂ inhibits the reaction. For both catalysts, the reaction kinetics are independent of the values of p_{NO_2} and p_{N_2} .

On the other hand, considerable differences have been found in the reaction temperatures and the apparent activation energies. These observations clearly indicate that the doping with platinum has a significant positive effect on the catalytic properties of LaMnO₃ perovskite in the reaction investigated.

As seen in Fig. 6, the conversion of NO decreases on changing the inlet NO : CO ratio from 1 : 1 to 1 : 2. Apparently, the activity of the platinum-doped catalyst is influenced by the composition of the inlet mixture. This phenomenon has already been observed with platinum catalysts and explained by changes in the oxidation state of platinum¹⁷. Platinum in a reduced valence state forms stronger bonds with adsorbed CO molecules, so hindering further reaction of CO with NO. In our platinum-doped perovskite, part of the platinum probably occurs on the surface in the metal state¹⁶. This portion of platinum may exhibit properties similar to those of platinum supported on an inactive carrier. However, despite the initial decrease in activity brought about by the increase in the CO : NO ratio, the catalyst retains its thermal stability and, as illustrated in Fig. 6, is still more active than pure LaMnO₃.

A requirement placed on detoxication catalysts is to speed up both the reduction of nitrogen oxide and the oxidation reactions. For this reason, the oxidation of CO by oxygen¹⁶ and the reduction of nitrogen oxide by carbon monoxide have been investigated at various concentrations of O₂. The obtained dependences of the NO conversion on the amount of oxygen in the reaction mixture or more precisely, on the ratio, *m*, of oxidating and reducing components defined by the relationship

$$m = (n_{\text{NO}} + 2n_{\text{O}_2})/n_{\text{CO}}, \quad (3)$$

TABLE II
Rate constants k_2 of Eq. (2) ($a = 1$) for the reduction of NO by CO over platinum-doped LaMnO₃ at various temperatures

t °C	k_2 mol h ⁻¹ g ⁻¹ . MPa ^{-0.073}	Estimate of dispersion, $k_2 \cdot 10^4$	Average relative error, r , %	Standard deviation $\cdot 10^3$
250	1.39	7.32	4.4	2.5
275	2.34	11.20	8.3	6.2
300	3.46	0.92	2.1	2.7
350	4.66	1.21	4.2	2.9
400	5.58	8.31	7.2	5.7

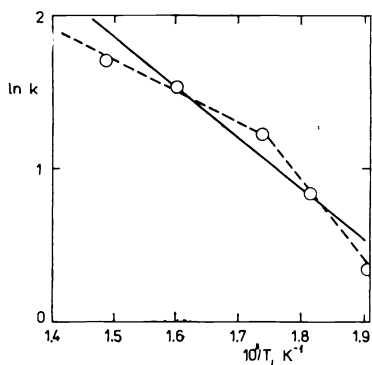


FIG. 5
Arrhenius dependence of the rate constant k_2 of Eq. (2) for LaMn_{0.99}Pt_{0.01}O₃

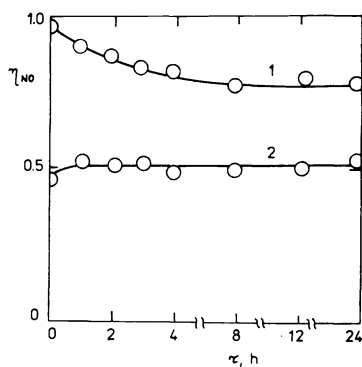


FIG. 6
Variation in NO conversion with time at NO : CO = 1 : 2, $W/F = 4 \text{ g h mol}^{-1}$, and $t = 350^\circ\text{C}$. Catalyst: 1 LaMn_{0.99}Pt_{0.01}O₃; 2 pure LaMnO₃

where n_{NO} , n_{O_2} and n_{CO} are the molar concentrations of the respective components in the inlet mixture, are represented in Fig. 7 for pure LaMnO_3 and in Fig. 8 for platinum-doped LaMnO_3 . When pure LaMnO_3 is used and the oxygen concentrations correspond to molar ratios from 1 to 1.25, oxygen promotes the $(\text{NO} + \text{CO})$ reaction only very weakly. At $m > 1.25$ oxidation of CO by oxygen occurs preferentially in the system and NO conversion decreases because of the consumption of CO in the oxidation.

A marked change in the behaviour of the system $\text{NO} + \text{CO} + \text{O}_2$ was observed when platinum-doped LaMnO_3 was used, as illustrated in Fig. 8. The addition of small amounts of oxygen resulted in a significant increase in NO conversion. Oxygen accelerated the reaction of NO with CO up to a concentration corresponding to $m = 1.57$.

Further increases in the excess of oxygen, i.e., the growth of the value of m , produced an appreciable decrease in the conversion of NO. Such a behaviour was observed at a temperature of 250°C . Figure 8 also shows that with increasing temperature the maximum on NO conversion shifts to lower values of m . The NO conversion vs m curves intersect at a point corresponding to $m = 1.8$ and an NO conversion of 42%. Hence it may be concluded that at $m > 1.8$ the predominating reaction is the oxidation of CO by oxygen. At $m < 1.8$, CO may be oxidized by both NO and oxygen. Thus acceleration of NO reduction depends on the value of m and the reaction temperature.

Alikina and co-workers¹⁷, who studied the same system using $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ as catalyst, arrived at similar conclusions. They found a variation in NO conversion

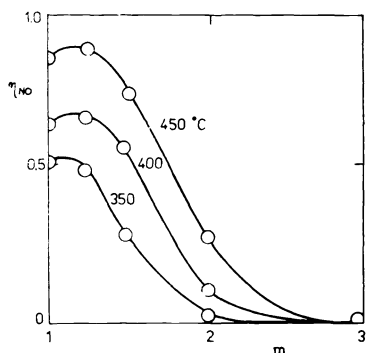


FIG. 7

Variation in NO conversion with molar ratio m in the system $\text{NO} + \text{CO} + \text{O}_2$ ($\text{NO} : \text{CO} = 1 : 1$) over LaMnO_3 at temperatures of 350, 400 and 450°C

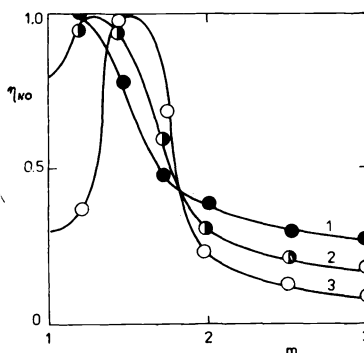


FIG. 8

Variation in NO conversion with molar ratio m in the system $\text{NO} + \text{CO} + \text{O}_2$ ($\text{NO} : \text{CO} = 1 : 1$) over $\text{LaMn}_{0.99}\text{Pt}_{0.01}\text{O}_3$. Temperature, $^\circ\text{C}$: 1 450; 2 350; 3 250

with the molar ratio m analogous to our results for platinum-doped LaMnO_3 except that they did not observe an effect of oxygen on the growth of NO conversion until at a temperature of 440°C and found a maximum in NO conversion at $m = 1.15$. As discussed previously¹⁶, platinum occurs in the perovskite not only as Pt^{4+} , but also as the platinum metal. The shift of the maximum in NO conversion for platinum-doped perovskite to lower temperatures than those found with the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst is probably due to the presence of Pt^{4+} , which is likely to be stabilized by the perovskite structure at B positions of the ABO_3 perovskite. The shift may also be influenced by the activity of the perovskite alone which may, from this point of view, be regarded as an active carrier. The question of relative proportions of these effects cannot be decided at present. Of fundamental importance, however, is the observation that the doping of LaMnO_3 perovskite with a small amount of platinum produces a catalytic material that is superior to platinum alone^{17,18}.

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