

Catalytic Oxidation of Carbon Monoxide on LnCoO₃ Perovskite Oxides

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The Kinetics of oxidation of CO from stoichiometric and other mixtures on LnCoO₃ (Ln = La, Nd, Gd) have been studied in the temperature range 150 to 300°C. The influence of initial total pressure and excess of CO and oxygen on the rate of reaction has been studied. On the basis of the kinetic analysis, it is proposed that the surfaces are saturated with respect to both the reactants at the early stages of the reaction when the reactants are present together and the ensuing surface reaction between the adsorbed species controls the overall reaction rate. The rate equation applicable for this process has also been deduced.

The catalytic activity variation for CO oxidation among LaMO₃ oxides showed (1) maxima for LaMnO₃ (d⁴) and LaCoO₃ (d⁶) thus leading to the importance of local symmetry considerations in deciding the observed catalytic activity. As a corollary to this analysis, Tascon and Tejuca (2) have concluded that the activation centers on LaCoO₃ catalyst are cobalt ions for oxygen and the oxide ions for CO and CO₂, while the La³⁺ ions are inactive for the catalytic oxidation of CO. On the other hand, it is known that the rare earth ions have considerable influence on the observed magnetic and electrical properties as well as the spin state of cobalt ions in LnCoO₃ type oxides (3) and hence they can be expected to exhibit different surface properties, especially when the catalyst has to function as an "electron relay switch" with the aid of the surface orbitals of suitable symmetry and proper energy. As a part of our attempt to address this question, we present in this communication the results of the kinetic studies on the oxidation of CO on LnCoO₃ (where Ln = La³⁺, Nd³⁺, and Gd³⁺).

EXPERIMENTAL

The kinetics of oxidation of CO were studied in an all glass recirculatory type of reactor

described elsewhere (4). The catalysts were prepared by heating the rare earth oxalate and cobalt oxalate at 900°C for 24 hr as described in literature and were characterized by X-ray diffraction patterns.

RESULTS AND DISCUSSION

On the basis of the results with mixed gas adsorption isotherms at subreaction conditions on LaCoO₃ (5), it is assumed that there is always attendant adsorption in stoichiometric proportion in addition to the surface reaction which accounted for the pressure changes experimentally observed. The regression procedure developed for analysis of kinetic data with attendant adsorption (6) has been utilized to evaluate the kinetic parameters pertaining to the oxidation reaction. In brief, the procedure adopted for correcting the pressure readings for simultaneous adsorption with attendant reaction is to treat the adsorption process to obey Elovich type kinetics and then suitably correct each of the pressure readings for simultaneous adsorption. Details of this correction procedure have been discussed in an earlier paper (6).

Generally, the experimental data thus corrected for concurrent adsorption obey a simple first-order equation, i.e., $\log p_0/p$ varies

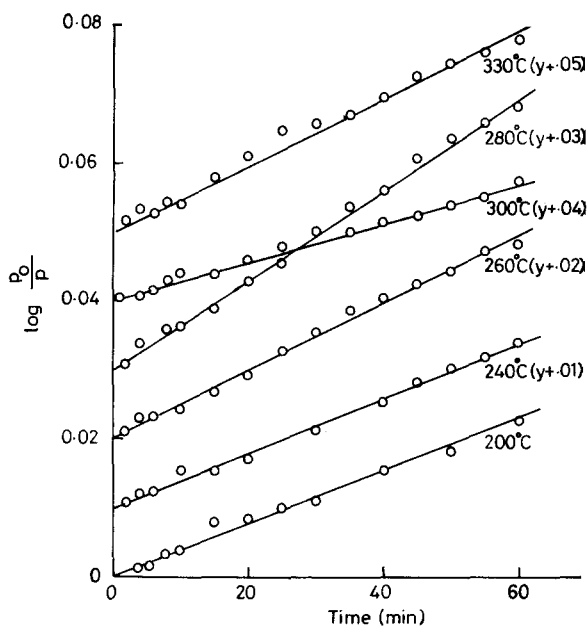


FIG. 1. Typical first-order plots for the oxidation of CO on NdCoO_3 (Origin shifted along y axis as indicated in parenthesis for clarity).

linearly with time where p is the total pressure at any time t and p_0 is the initial total pressure. Typical plots treated in terms of first-order equation are given in Fig. 1 for the oxidation of CO on NdCoO_3 in the temperature range 200 to 360°C. The Arrhenius parameters deduced are given in Table I. It is seen that the Arrhenius plot for NdCoO_3 showed a gradient change around 280°C, thus giving rise to two sets of values for Arrhenius parameters. It is known that the adsorption isobars of oxygen and CO show maxima around 300°C (7) and if the reaction were to be controlled by interaction between the adsorbed species, then by virtue of the changes in the modes of adsorption of both the components one can expect a change in the activation parameters. However, it is observed only in the case of NdCoO_3 , since this temperature range is crossed only in this case. The values of Elovich parameters deduced from the data for concurrent adsorption on NdCoO_3 show an abrupt change around 280°C supporting this conclusion (see Table II). The logarithm of the first-order rate con-

stant values evaluated from analysis of data at various initial total pressures (p_0) were found to vary inversely (slope = -1) with the logarithm of the total initial pressure (p_0) showing that the apparent rate constants can be expressed by an equation $k = k'/p_0^n$ where k' is the true rate constant independent of initial pressure conditions. These results are in complete conformity with the earlier observations on LaCoO_3 (5).

TABLE I
Arrhenius Parameters for the Oxidation of CO on
Rare Earth Cobaltites^a

Catalyst	Temperature range (°C)	Activation energy (kcal/mol)	k_0 (min^{-1})
LaCoO_3	140–280	3.4	4.6×10^{-2}
GdCoO_3	180–260	9.8	1.9×10^1
NdCoO_3	200–280	6.4	3.8×10^{-1}
	300–360	12.1	1.8×10^2

^a The rate constant values were evaluated from kinetic data at a total pressure of around 60 Torr of stoichiometric mixtures of CO + O₂ (2:1) and on 2 g of the catalyst.

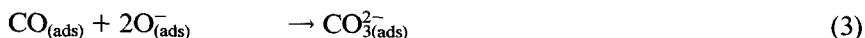
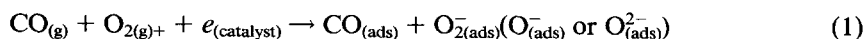
TABLE II
Elovich Parameters for the Concurrent Adsorption with Reaction in the
Oxidation of CO on LnCoO₃ Type Oxides

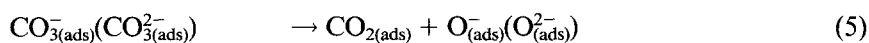
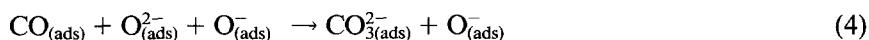
Catalyst/total pressure/ temperature	Temperature/ total pressure	t ₀ (min)	α	Amount adsorbed in pressure units (Torr)
LaCoO ₃ 60 Torr	140°C	0.33	45.5	1.72
	150°C	0.33	83.3	0.86
	180°C	0.33	58.8	1.32
	220°C	0.33	50.0	1.27
	240°C	0.33	66.6	0.66
	280°C	0.33	66.6	1.77
LaCoO ₃ 180°C	37.6 Torr	0.21	66.6	
	54.2 Torr	0.33	58.8	
	81.5 Torr	0.45	40.0	
NdCoO ₃ 56.5 Torr	200°C	0.33	25.0	3.12
	240°C	0.33	27.0	2.89
	260°C	0.33	33.3	2.03
	280°C	0.33	58.8	1.04
	300°C	0.33	33.3	1.42
NdCoO ₃ 200°C	40.9 Torr	0.24	66.6	
	46.5 Torr	0.27	37.0	
	56.7 Torr	0.33	25.0	
	61.6 Torr	0.36	35.7	
	70.6 Torr	0.41	38.5	
NdCoO ₃ 200°C	101.9 Torr	0.59	20.8	
	6CO:4O ₂ :2He	0.33	52.6	1.35
	4CO:4O ₂ :4He	0.33	58.8	1.32
	2CO:4O ₂ :6He	0.33	71.4	0.94
	8CO:3O ₂ :1He	0.33	40.0	1.94
	8CO:2O ₂ :2He	0.33	47.6	1.62
56.5 Torr	8CO:1O ₂ :3He	0.33	111.1	0.70

Tascon and Tejuca (7) have studied the adsorption of the individual components of the reactions on LaCoO₃. Their data show that activated adsorption of CO or oxygen occurs above 298 and 423°K, respectively. The reaction temperature ranges chosen in this study therefore refer to a region where activated adsorption of both the components takes place. Tascon and Tejuca (7) have also recorded that adsorption of oxygen on Co²⁺ results in the formation of O₂⁻ species which probably rapidly transforms to O²⁻ through

O⁻. If it is assumed that CO is adsorbed on oxide ions then there can be more than one type of carbonate species formed with different types of adsorbed oxygen species, the relative concentration of which is dependent on temperature and hence can account for the gradient change in the Arrhenius plot for NdCoO₃ around 280°C.

The results obtained in the present study lead to the formulation of the following mechanism for the oxidation of CO on LnCoO₃ oxides





where (g) and (ads) refer to gas phase and adsorbed states. In this reaction sequence any one of the reaction steps between the adsorbed species (steps 2–4) could be rate controlling. It is generally considered (8) that the lattice oxide ions do not participate in complete combustion and that the adsorbed oxygen species alone are responsible for the total oxidation reaction. On this basis one may presume that either step (2) or (3) involving the adsorbed oxygen species is the probable rate-controlling pathway for the surface reaction.

On the basis of the values of true rate constants evaluated from $\log p_0$ tending to zero in the plot of $\log k$ vs $\log p_0$ (see Table III) it can be concluded that the activity order is $\text{GdCoO}_3 > \text{LaCoO}_3 > \text{NdCoO}_3$. It must be remarked that Rao *et al.* (9) have observed that NdCoO_3 and HoCoO_3 showed the highest activity which has been attributed to the relative population of high spin Co^{3+} ions compared to that of other spin states. The mechanism proposed by them involves the participation of lattice oxide ions, which is not in agreement with the recent analysis by Tascon *et al.* (10).

The effect of the product CO_2 on the rate of the reaction has been evaluated using the same partial pressure of CO and oxygen and evaluating the first-order rate constants in the presence of helium or CO_2 . These studies

show that CO_2 has an inhibition effect. The inhibiting effect could be due to CO_2 competing for adsorption sites with CO as reported by Tascon and Tejuca (2). In the rate expression given above the term which accounts for CO_2 inhibition does not appear as this term is negligible in comparison to the other terms as the amount of CO_2 produced is small.

The analysis of the kinetic data with mixtures other than stoichiometry indicates the following:

(1) The amount of $\text{CO} + \text{O}_2$ adsorbed is maximum for stoichiometric mixtures and is decreased when mixtures other than stoichiometry are used (Table II).

(2) The initial conditions either in the form of excess oxygen or excess CO affect the determination of the true rate constant for the reaction and the apparent rate constants obtained from simple first-order plots varies with the partial pressures of CO/O_2 depending on which one is varied.

(3) The initial rate of the reaction varies linearly with p_{CO} while a linear relationship is obtained between $(p_{\text{O}_2}/r_a)^{1/2}$ vs $p_{\text{O}_2}^{1/2}$ where r_a is the initial rate, showing that at time $\rightarrow 0$ the rate of the reaction is controlled by the surface coverage of $\text{CO}(\theta_{\text{CO}})$ or of $\text{O}_2(\theta_{\text{O}_2})$.

(4) On the basis of all these results the rate law applicable for the oxidation of CO on LnCoO_3 oxides is deduced to be

$$r = \frac{k\theta_{\text{CO}}\theta_{\text{O}_2}}{p_0^a(1 + p'_{\text{O}_2})^m(1 + p'_{\text{CO}})^l}$$

where p'_{CO} and p'_{O_2} refer to excess partial pressures of CO and oxygen and p_0 is the total initial pressure. This equation is similar to the one used by Yao (11) for the oxidation of CO on LaCoO_3 except for the differences

TABLE III

The Values of First-Order Rate Constants for the Oxidation of CO on LnCoO_3 at $\log p_0 \rightarrow 0$

Catalyst	$k \times 10^{-2} \text{ (min}^{-1}\text{)}$
LaCoO_3	4.17
NdCoO_3	2.09
GdCoO_3	51.92

in the values of powers of p_{CO} and p_{O_2} which could be due to the differences in the experimental procedures employed. A similar rate expression has also been used by Tascon *et al.* (10) for treating the kinetics of oxidation of CO on LaCoO_3 .

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