

## CO OXIDATION ON $\text{LnCoO}_3$ PEROVSKITE OXIDES: EFFECT OF INITIAL TOTAL PRESSURE AND GAS COMPOSITION

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(Received January 26, 1983)

### Summary

The kinetics of oxidation of CO on  $\text{LnCoO}_3$  ( $\text{Ln} \equiv \text{La, Nd, Sm, Gd}$ ) were studied in the temperature range 150 - 360 °C. These systems show an abrupt gradient change in the Arrhenius plots for CO oxidation at about 200 °C. The adsorption isobars constructed for the total amount of gas mixture adsorbed show either a maximum or a minimum at the same temperature, indicating that the change in the mode of adsorption of the reactants is the cause for the break in the Arrhenius plots. The effect of the initial total pressure and an excess of CO or oxygen on the rate of the reaction was studied and the intrinsic rate constants were calculated.

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Rare earth-cobalt oxide compounds have been explored for many technical applications, e.g. as electrodes in fuel cells [1] and as autoexhaust conversion catalysts [2, 3]. In an earlier investigation [4] it was observed that CO and oxygen were adsorbed in stoichiometric proportions (2 parts CO to 1 part oxygen) when present together on  $\text{LaCoO}_3$ . These systems also showed abrupt gradient changes in the Arrhenius plots (Fig. 1) for the oxidation of CO at about 200 °C [5]. This could be associated with the ordering of high spin and low spin cobalt ions on two sublattices, which usually takes place in the range 450 - 650 K. However, this explanation is not substantiated by the results of the present investigation. The purpose of this paper is to provide further evidence for these two observations and to identify the possible active sites for the oxidation of CO on  $\text{LnCoO}_3$  (where  $\text{Ln} \equiv \text{La, Nd, Sm, Gd}$ ).

The catalysts were prepared by heating the rare earth oxalate with cobalt oxalate in stoichiometric proportions at about 900 °C for 24 h, and they were characterized by means of X-ray diffraction. The kinetics of oxidation of CO were studied in an all-glass recirculatory type of reactor described elsewhere [6].

It was observed that, during the catalytic oxidation reaction, there is attendant adsorption of the reactants in stoichiometric proportions. A

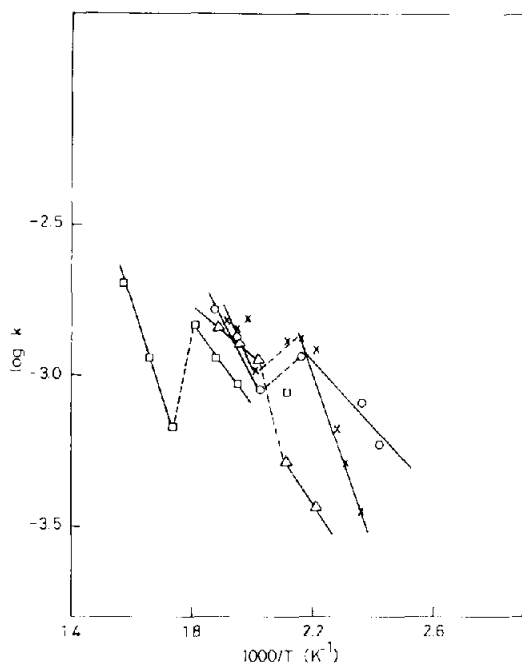


Fig. 1. Arrhenius plots for the oxidation of CO on  $\text{LnCoO}_3$ :  $\circ$ ,  $\text{LaCoO}_3$ :  $\square$ ,  $\text{NdCoO}_3$ :  $\times$ ,  $\text{SmCoO}_3$ :  $\triangle$ ,  $\text{GdCoO}_3$ .

regression procedure was used to correct the kinetic data for attendant adsorption [7]; the adsorption process was assumed to obey Elovich-type kinetics. The kinetic data thus corrected for attendant adsorption were found to obey a simple first-order equation as can be seen from the typical results given in Fig. 2. The adsorption isobars constructed for the total amount of gas mixture adsorbed are shown in Fig. 3. It is seen that the isobars show either a maximum or a minimum corresponding to the temperatures where gradient changes were observed in the Arrhenius plots, showing that the change in the mode of adsorption of the reactants is the cause for the break in the Arrhenius plots.

It is observed that the apparent rate constants calculated from the first-order plots for the oxidation reaction from stoichiometric mixtures at any given temperature are dependent on the total initial pressure as revealed from the data given in Table 1. However, the true rate constants, evaluated from the values of the apparent rate constants accounting for the variation in the initial total pressure [4], are found to be almost constant and probably not dependent on the rare earth ion present in the  $\text{LnCoO}_3$  system.

The values of the apparent first-order rate constants were evaluated using various compositions of CO and oxygen other than the stoichiometric composition; the temperature and the total initial pressure were held constant. It is seen (typical data for  $\text{NdCoO}_3$  and  $\text{SmCoO}_3$  are given in Table 2) that the values of the apparent rate constants are highest for the stoi-

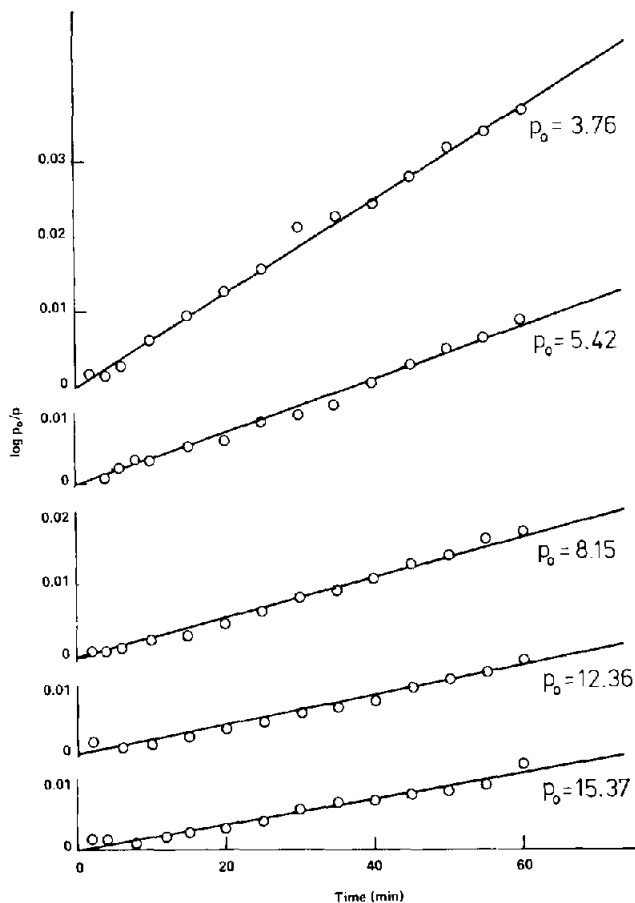


Fig. 2. Typical first-order plots for the oxidation of CO on  $\text{LaCoO}_3$ .

chiometric mixtures. The presence of either an excess of CO or an excess of oxygen results in lower values for the apparent first-order rate constants.

In order to obtain the values of the intrinsic rate constants and to take into account the effect of the initial total pressure and that of an excess of one of the reactants, experiments were carried out in which the partial pressure of one of the components was kept constant and the partial pressure of the other component was varied; helium was used to maintain a constant initial total pressure. It is seen that the values of the intrinsic rate constants calculated using the expression

$$k' = kp_0(1 + p_{\text{O}_2}') (1 + p_{\text{CO}}')$$

(where  $k$  and  $k'$  are the apparent and intrinsic rate constants,  $p_{\text{O}_2}'$  and  $p_{\text{CO}}'$  refer to the excess partial pressure of oxygen and CO over that for the stoichiometric composition and  $p_0$  is the initial total pressure) are not depen-

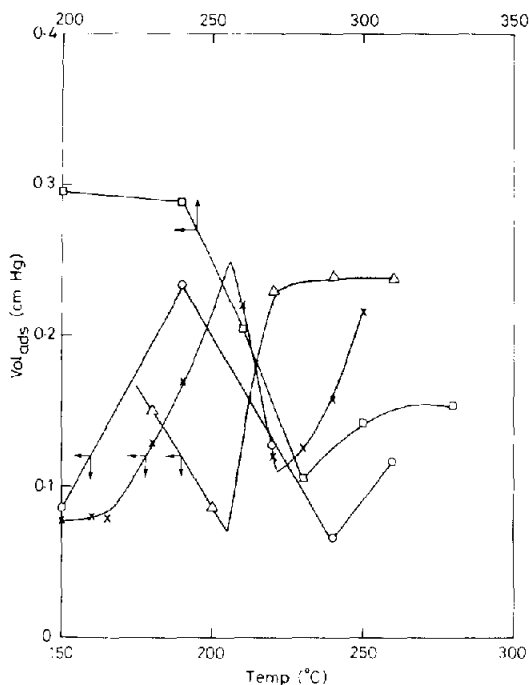


Fig. 3. Adsorption isobars for the adsorption of mixtures of CO and oxygen on  $\text{LnCoO}_3$ :  $\circ$ ,  $\text{LaCoO}_3$ ;  $\square$ ,  $\text{NdCoO}_3$ ;  $\times$ ,  $\text{SmCoO}_3$ ;  $\triangle$ ,  $\text{GdCoO}_3$ .

dent on the composition of the gas mixture (typical data for  $\text{NdCoO}_3$  are given in Table 3).

The above results indicate the following.

(i) The active sites in all these catalysts are the same, probably the oxide ions for CO activation and the cobalt ions for oxygen activation. The rare earth ion seems effectively not to participate in the catalytic oxidation reaction. This deduction is in agreement with the conclusions of Tascon *et al.* [7].

(ii) The composition of the adsorbed state is always stoichiometric and the presence of an excess of either component effectively decreases the extent of the surface coverage and hence results in a lower value for the apparent first-order rate constant.

(iii) The intrinsic activity of the active surface sites appears not to be dependent on the properties of the system as it is known [8] that these systems contain varying proportions of high and low spin cobalt(III) as well as other cation sites. However, this deduction has to be substantiated by further experimental data.

TABLE I  
 Apparent and intrinsic first-order rate constants as functions of the initial total pressure for the oxidation of CO on  $\text{LnCoO}_3$

Values for CO oxidation on $\text{LaCoO}_3$			Values for CO oxidation on $\text{NdCoO}_3$			Values for CO oxidation on $\text{SmCoO}_3$			Values for CO oxidation on $\text{GdCoO}_3$		
Initial total pressure $P_0$ (cmHg)	Apparent rate constant $k$ ( $\times 10^{-4}$ min $^{-1}$ )	Intrinsic rate constant $k'$ ( $\times 10^{-3}$ cmHg min $^{-1}$ )	Initial total pressure $P_0$ (cmHg)	Apparent rate constant $k$ ( $\times 10^{-4}$ min $^{-1}$ )	Intrinsic rate constant $k'$ ( $\times 10^{-3}$ cmHg min $^{-1}$ )	Initial total pressure $P_0$ (cmHg)	Apparent rate constant $k$ ( $\times 10^{-4}$ min $^{-1}$ )	Intrinsic rate constant $k'$ ( $\times 10^{-3}$ cmHg min $^{-1}$ )	Initial total pressure $P_0$ (cmHg)	Apparent rate constant $k$ ( $\times 10^{-4}$ min $^{-1}$ )	Intrinsic rate constant $k'$ ( $\times 10^{-3}$ cmHg min $^{-1}$ )
3.76	13.9	5.2	4.10	11.4	4.7	3.66	12.6	4.6	4.66	14.0	6.5
5.42	7.9	4.3	4.65	11.2	5.2	4.92	12.4	6.1	7.97	7.7	6.1
8.15	5.8	4.8	6.16	9.2	5.7	5.60	12.1	6.8	9.50	5.1	4.9
12.36	4.2	5.2	7.06	8.8	6.2	6.97	7.3	5.1	11.24	4.4	5.0
15.37	3.5	5.3	10.19	6.4	6.5	7.33	8.9	6.5			
Average		5.0			5.7			5.8			5.6

TABLE 2

Values of the apparent first-order rate constants as functions of the composition of the reaction mixture for oxidation of CO on  $\text{LnCoO}_3$  at an initial total pressure of about 60 Torr

Values for CO oxidation on $\text{NdCoO}_3$ at 200 °C		Values for CO oxidation on $\text{SmCoO}_3$ at 180 °C	
Composition of reaction mixture	Apparent rate constant $k$ ( $\times 10^{-4} \text{ min}^{-1}$ )	Composition of reaction mixture	Apparent rate constant $k$ ( $\times 10^{-4} \text{ min}^{-1}$ )
2.65CO:1.0O <sub>2</sub>	6.2	2.50CO:1.0O <sub>2</sub>	7.4
2.25CO:1.0O <sub>2</sub>	5.6	2.25CO:1.0O <sub>2</sub>	8.1
2.00CO:1.0O <sub>2</sub>	8.5	2.00CO:1.0O <sub>2</sub>	12.1
2.00CO:1.1O <sub>2</sub>	6.3	2.00CO:1.5O <sub>2</sub>	7.2
2.00CO:1.3O <sub>2</sub>	6.1	2.00CO:2.0O <sub>2</sub>	7.5
2.00CO:1.5O <sub>2</sub>	6.3		

TABLE 3

Values of the apparent and the intrinsic first-order rate constants as functions of the composition of the reaction mixture for oxidation of CO on  $\text{NdCoO}_3$  at 200 °C

Composition of reaction mixture	Excess partial pressure of CO or O <sub>2</sub> over that for the stoichiometric composition (cmHg)	Initial total pressure (cmHg)	Apparent rate constant $k$ ( $\times 10^{-4} \text{ min}^{-1}$ )	Intrinsic rate constant $k'$ ( $\times 10^{-3} \text{ cmHg}^n \text{ min}^{-1}$ ) <sup>a</sup>
8CO:1O <sub>2</sub> :3He	2.86	5.73	1.9	4.3
8CO:2O <sub>2</sub> :2He	1.92	5.76	3.1	5.3
8CO:3O <sub>2</sub> :1He	0.95	5.67	4.7	5.2
8CO:4O <sub>2</sub>	—	5.67	9.8	5.6
6CO:4O <sub>2</sub> :2He	0.46	5.58	9.0	6.1
4CO:4O <sub>2</sub> :4He	0.95	5.71	7.1	5.7

<sup>a</sup> The exponent  $n$  has the following values: for  $p_{\text{CO}}:p_{\text{O}_2} > 2$ ,  $n = 1$ ; for  $p_{\text{CO}}:p_{\text{O}_2} < 2$ ,  $n = 0.5$ ; for  $p_{\text{CO}}:p_{\text{O}_2} = 2$ ,  $n = 0$ .

### Acknowledgment

The authors are grateful to the University Grants Commission, New Delhi, for the award of a teacher fellowship to one of them (S.G.).

### References

- 1 D. B. Meadowcraft, *Nature (London)*, 226 (1970) 847.
- 2 S. C. Sorenson, J. A. Wronkiewicz, L. B. Sis and G. P. Writz, *Am. Ceram. Soc., Bull.*, 53 (1974) 446.

- 3 O. Parkash, P. Ganguly, G. Ramarao, C. N. R. Rao, D. S. Rajoria and V. G. Bhide, *Mater. Res. Bull.*, 9 (1974) 1173.
- 4 S. George, B. Viswanathan and M. V. C. Sastri, *Indian J. Chem., Sect. A*, 15 (1977) 285.
- 5 S. George and B. Viswanathan, *Proc. 1st Natl. Workshop on Catalysis, Dhanbad, December 10 - 12, 1981*, Catalysis Society of India, Madras, 1981, p. 80.
- 6 K. R. Krishnamurthy, B. Viswanathan and M. V. C. Sastri, *Proc. Indian Natl. Sci. Acad., Part A*, 43 (1977) 34.
- 7 J. M. D. Tascon, J. L. G. Fierro and L. G. Tejuca, *Z. Phys. Chem. N.F.*, 124 (1981) 249.
- 8 C. N. R. Rao, *J. Indian Chem. Soc.*, 51 (1974) 979.