

Kinetics of Oxidation of Carbon Monoxide on Lanthanum Cobaltite

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Adsorption of CO and O₂ has been studied on a lanthanum cobaltite catalyst in a standard volumetric adsorption apparatus. It is found that the catalyst does not adsorb either CO or O₂ separately but adsorbs both the gases from a mixture of the two. The kinetics of the oxidation of CO over LaCoO₃ has been investigated in an all glass recirculatory type of reactor. The reaction is found to follow the kinetic equation for a total order equal to one but the initial partial orders for both CO and O₂ are zero. Hence, it is suggested that the reaction occurs between the adsorbed species, the catalyst surface being continuously saturated by the reactants and inhibited by the carbon dioxide produced.

FOLLOWING the original suggestion by Libby¹ that LaCoO₃ can be a good catalyst for automobile exhaust pollution control, various substituted and unsubstituted rare earth transition metal oxides having the perovskite structure have been shown to be good catalysts for the oxidation of carbon monoxide and hydrocarbons²⁻⁵. Extensive studies⁶ have been carried out in evaluating the perovskite type oxides as oxidation catalysts under various experimental conditions like (i) varying the composition of the catalyst, (ii) varying the thermal treatment of the oxides and (iii) in presence of SO₂ and sulphur-free environment. As a part of the effort undertaken to evaluate the kinetic parameters of the CO oxidation over various catalysts under different conditions, a study of the oxidation of CO on LaCoO₃ has been carried out.

Materials and Methods

LaCoO₃ catalyst was prepared by heating lanthanum oxalate and cobalt oxalate at 900° for 23 hr.

Adsorption measurements were carried out in a standard volumetric adsorption apparatus using a Fischer gas partitioner model 29 (Fischer Hamilton Co., USA) for the *in situ* analysis of gas mixtures.

The kinetics of oxidation of CO were studied in an all glass recirculatory type of reactor described elsewhere⁷.

Results

It was found that though the catalyst did not adsorb, even minutely, either carbon monoxide or oxygen separately, it adsorbed both the components together when exposed to a mixture of carbon monoxide and oxygen. The mixed gas adsorption isotherms at non-reaction temperatures are given in Figs. 1 and 2.

The kinetics of oxidation of CO were studied under the following conditions: (i) at constant total initial pressures, either at 60 or 100 torr, but varying the

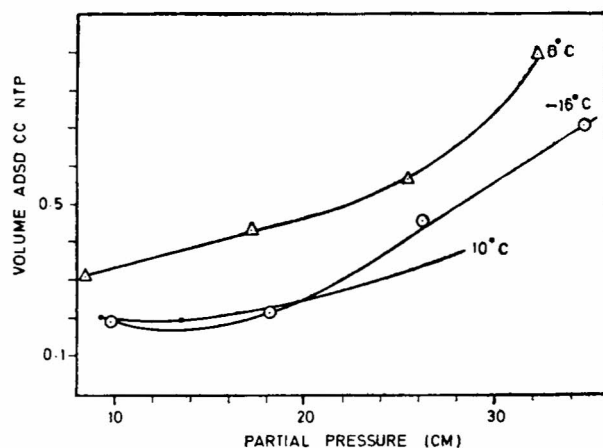


Fig. 1 — Adsorption isotherms of CO on LaCoO₃ from CO:O₂ mixture (2:1)

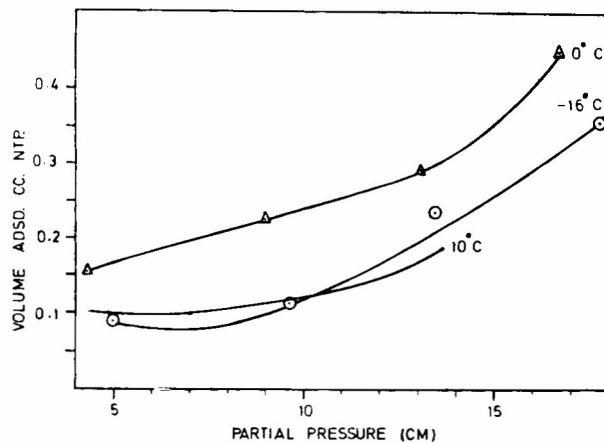


Fig. 2 — Adsorption isotherms of O₂ on LaCoO₃ from CO:O₂ mixture (2:1)

temperature; and (ii) at constant temperature but varying the composition of the gas mixtures.

Typical kinetic plots at various temperatures at an initial total pressure of 60 torr are given in Fig. 3 and the corresponding plots at 190° for varying

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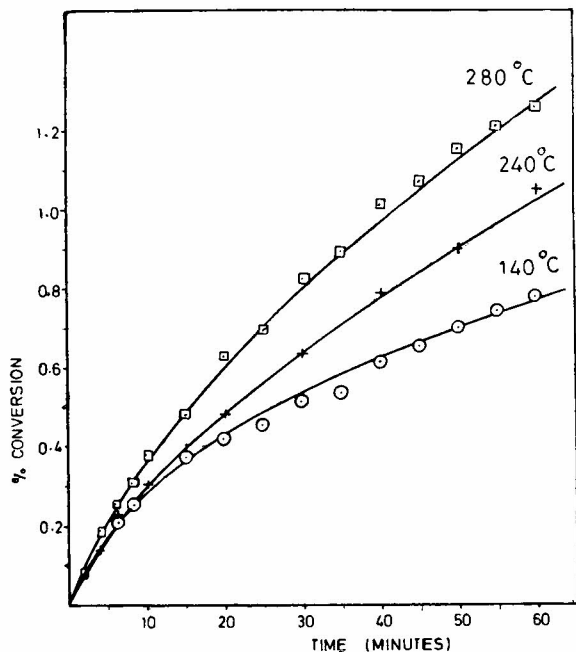


Fig. 3 — Percentage conversion at different temperatures at an initial pressure of 60 torr

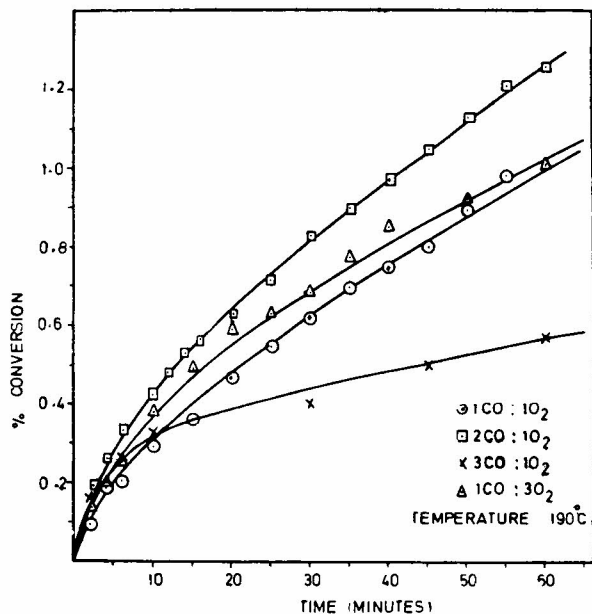


Fig. 4 — Percentage conversion at different CO: O₂ mixtures at constant temperature

compositions of the gas mixtures are presented in Fig. 4.

It is seen from Fig. 5 that the experimental data follow the kinetic equation for the total order equal to one, i.e. $\log p_0/p$ varies linearly with t , where p is the total pressure at time t and p_0 is the initial total pressure. The partial orders with respect to the concentration of carbon monoxide and oxygen in non-stoichiometric mixtures are then established, by fitting the data in the equation

$$dp_{CO_2}/dt = k p_{CO}^x p_{O_2}^y; x + y = 1$$

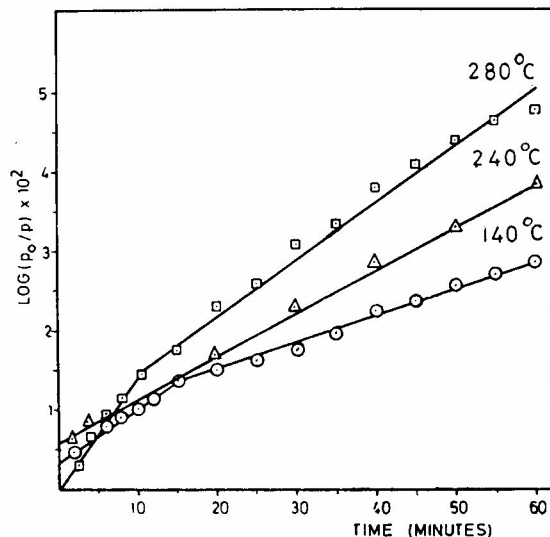


Fig. 5 — First order kinetic plots at different temperatures

These experiments were carried out at various temperatures on the same catalyst and the values of the initial rates are given in Table 1.

TABLE 1 — KINETIC DATA FOR OXIDATION OF CO ON LaCoO₃

Mixture (CO:O ₂)	Total initial pressure (in mm Hg)	p_{CO} (mm Hg)	p_{O_2} (mm Hg)	Initial rate (mm Hg/min)
TEMP. 190°				
1: 1	61.0	30.5	30.5	0.024
2: 1	62.0	41.3	20.7	0.021
3: 1	59.2	44.4	14.8	0.022
TEMP. 150°				
1: 1	59.6	28.8	28.8	0.028
2: 1	61.1	40.7	20.4	0.030
3: 1	59.0	44.3	14.7	0.030
TEMP. 280°				
1: 1	58.9	29.45	29.45	0.035
2: 1	60.0	40.0	20.0	0.036
3: 1	59.4	44.6	14.8	0.038

Excess of either carbon monoxide or oxygen had no influence on the initial rate, indicating that the initial (zero time) partial orders are zero for both the reactants. Hence, the total order of one exhibited with respect to time, is an apparent order. Table 2 gives the values of the initial experimental rates for different total pressures of the stoichiometric mixtures. If the order one, during the reaction, were a true one, the initial rate should be proportional to the initial total pressure according to $(dp_{CO_2}/dt)_{t=0} = k p_0^m$.

The values in Table 2 show that the initial rate is a constant, unaffected by the initial total pressure. The true order at time zero is determined by

TABLE 2 — INITIAL RATES AT 90° FOR STOICHIOMETRIC MIXTURES

p_0 (mm Hg)	Initial experimental rate (mm Hg/min)
49.0	0.075
61.7	0.08
105.5	0.085
200.6	0.075

 TABLE 3 — EFFECT OF CO₂ REMOVAL ON THE INITIAL RATES

Temp. °C	Initial rate with trap (mm Hg/min)	Initial rate without trap (mm Hg/min)
190	0.04	0.02
240	0.09	0.04
280	0.05	0.036

plotting the logarithm of the initial rate of Table 2 as a function of the logarithm of the initial pressure p_0 . The slope of this line gives a value $m=0.1 \approx 0$ for the initial true order. But this value does not arise out of a compensation between two partial orders of opposite sign.

The kinetic data obtained at 190° for stoichiometric mixtures by varying the initial total pressure from 3 to 15 cm Hg were analysed by plotting $\log p_0/p$ vs t . From the initial slopes of these plots the values of the rate constant ($k = \text{slope}/2.303$) were deduced. The logarithm of the rate constant was then plotted against logarithm of p_0 and its slope gave a value of $n = 1$ and this can be expressed by the equation $k = k'/p_0^n$, where k' is the true rate constant, independent of the initial conditions. The instantaneous rate at any moment for the first order kinetics is therefore given by

$$dp_{\text{CO}_2}/dt = kp = k'p/p_0^n$$

and, in particular at zero time, the total order is m .

The explanation for a catalytic reaction exhibiting initially and during the process the total and partial orders = zero, is that the reaction occurs between the adsorbed species and the catalyst surface is being continuously saturated by the reactants. This condition is applicable for zero time only. At any

definite time t , despite the surface saturation, the rate decreases according to the first order law instead of remaining constant. This could be due to the carbon dioxide produced inhibiting the rate of the reaction, as seen from the results for the reaction with and without a cold trap at liquid nitrogen temperature to remove the CO₂ formed (Table 3).

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