Catalytic Oxidation of Carbon Monoxide on LnCoO₃ Perovskite Type Oxides

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The kinetics of oxidation of CO has been studied on LnCoO₃ (Ln = La, Nd, Sm or Gd) oxides in the temperature range 150-360°C. The analysis of kinetic data and conductivity measurements reveal that the surface reaction between adsorbed species controls the overall reaction rate. A probable mechanism involving carbonate intermediates consistent with kinetic and electrical conductivity data has been proposed.

Perovskite type oxides have been investigated in recent years for possible application as electrodes in fuel cells¹ and in photoelectrochemical cells², and also as catalysts for oxidation and other reactions³. Among the available ABO₃ type perovskites, LnCoO₃ type compounds have received considerable attention for carbon monoxide oxidation for a variety of reasons⁴-⁷. Interestingly the activation centres on LaCoO₃ for CO oxidation are considered⁷ to be the cobalt ions for oxygen and the oxide ions for CO and CO₂ while the La³⁺ ions are inactive. This is surprising since it is known⁵ that the rare earth ions have considerable influence on the solid state properties as well as spin state of cobalt ions in LnCoO₃ oxides. Against this background, we present in this paper the results of the kinetic studies of oxidation of CO on LnCoO₃ oxides where Ln = La, Nd, Sm or Gd.

Materials and Methods

The catalysts were synthesised by heating the respective oxalates at 900°C for 24 hr and were characterised by X-ray diffraction. The kinetics of oxidation of CO was studied in an all glass recirculatory type of reactor described elsewhere⁸. The in situ electrical conductivity measurements were carried out in a specially designed two-probe cell.

Results and Discussion

Kinetic studies

As it has been observed that there is attendant adsorption in stoichiometric proportion⁹ in addition to surface reaction, the regression procedure developed for analysis of kinetic data with attendant adsorption¹⁰ has been utilised to evaluate the kinetic parameters of the oxidation reaction. The experimental data corrected for concurrent adsorption is found to obey a simple first order equation, that is log p₀/p varies linearly with t, where p is the total pressure at any time t after adsorption correction and p₀ is the initial total pressure. Typical first order plots are given in Fig. 1 for the oxidation of CO on GdCoO₃ in the temperature range 180-260°C. The Arrhenius parameters deduced from the Arrhenius plots (Fig. 2) are given in Table I. The Arrhenius plots show gradient changes in the temperature range 190-220°C; and the adsorption isobars of oxygen and CO show a maximum or minimum¹¹ in this temperature range. These observations are suggestive of a change in the mode of adsorption in this temperature range. This is also supported by the Elovich parameters deduced from the treatment of concurrent adsorption with reaction¹². If the reaction were to be controlled by the interaction between the adsorbed species, then the changes in the adsorption mode can be expected to alter the observed reaction rates as well as the reaction rate constants.

Fig. 1—First order plots for the oxidation of CO on GdCoO₃
Tascon et al.\textsuperscript{13} have recorded that the adsorption of oxygen on cobalt ions results in the formation of $O_2^-$ species which probably rapidly transforms to $O^2-$ through $O^-$, and the CO adsorbs on oxide ions resulting in different types of carbonate species. The relative concentration and nature of these active carbonate species will be dependant on temperature and hence could account for the gradient changes in the Arrhenius plots.

**Mechanism**

The results obtained in the present study lead to the mechanism of oxidation of CO on LnCoO$_3$ oxides as shown in Scheme 1, where (g), (l) and (ads) refer to the gas phase, lattice and adsorbed states respectively. In this reaction sequence any one of the reaction steps (2-4), between the adsorbed species can be rate-controlling. It is known\textsuperscript{14} that lattice oxide ions do not favour total oxidation reaction and the adsorbed oxygen species are responsible for complete oxidation.

The support for this mechanism is obtained from conductivity measurements under reaction conditions as well as in ambient conditions.

**Conductivity measurements**

It is seen that there is no change in conductivity with time in the case of LaCoO$_3$ and GdCoO$_3$ in the presence of CO or CO$_2$ on the evacuated catalysts as well as in the presence of CO alone or CO and O$_2$ on oxygen pretreated surface (see Figs 3 and 4). In order to monitor the effect of oxygen, the variation in conductivity as a function of equilibrium pressure of oxygen has also been measured, and the results are plotted in Figs 3 and 4 for LaCoO$_3$ and GdCoO$_3$ catalysts respectively. It is seen that after $\sim$ 35-40 torr

![Fig. 3 - Conductivity changes in ambient atmospheres on LaCoO$_3$](image_url)
of oxygen pressure, increase in conductivity is observed under equilibrium conditions. Normally these LnCoO$_3$ systems show an increase in conductivity as a function of temperature and become metallic at higher temperatures. The observation that there is no change in conductivity in the presence of either CO or CO$_2$ alone shows that CO and CO$_2$ are not adsorbed if present alone or if adsorbed do not involve any charge transfer process. The evacuated catalyst, which could be deficient in oxygen, takes up oxygen showing a decrease in conductivity at the initial stages. This initial decrease could be ascribed to fast adsorption process while the latter increase in conductivity could be associated with the transformation of adsorbed oxygen species to the lattice species. In the oxidised state, probably the system tends towards metallic behaviour. The conductivity changes observed with either oxygen alone or CO and oxygen mixture have to be ascribed to charge trapping by oxygen. The increase in conductivity after 35-40 torr of oxygen pressure shows the extent of oxygen species required for oxidising the reduced surface. This is a measure of the effect of extent of surface coverage on kinetics of transformation of adsorbed oxygen into lattice oxide ions. Therefore, mechanistically the reaction can either involve the charged adsorbed oxygen species and/or the transformed lattice oxide ions for the conversion of CO to CO$_2$. This conclusion is in agreement with the mechanism shown in Scheme 1.

It is seen from the values given in Table I that the activity order is not in accordance with the relative population of high spin Co$^{3+}$ ions in these systems. If it were to be so, then NdCoO$_3$ should have exhibited the highest activity.

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References

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