Catalytic Properties of Transition Metal Oxide Perovskites

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The catalytic activity of a series of perovskites such as LaCo$_{1-x}$Ni$_x$O$_3$ and LaCo$_{1-x}$Fe$_x$O$_3$ has been investigated for the oxidation of ethyl alcohol. It has been found that low-spin transition metal ions favour the oxygen transfer process responsible for oxidation. In nickel-rich compounds the activity of the catalyst is related to its ability to lose oxygen near the reaction temperature. Electrical resistivity studies show that surface oxygen ions are involved in the oxygen transfer reaction.

PEROVSKITE oxides of the formula (Ln, M)BO$_3$ and LnBO$_3$ where Ln is a trivalent rare earth ion, M a divalent cation, and B a transition metal ion, are found to be excellent catalysts for oxidation reactions. Electrical and magnetic properties of these compounds have been studied in detail. The LnBO$_3$ compounds show localized or itinerant behaviour of d-electrons depending on the spin configuration of the transition metal ion, low-spin ions being generally associated with itinerant d-electrons (as in LaNiO$_3$ and LaTiO$_3$) and high-spin ions (as in LaMnO$_3$ and LaFeO$_3$) with localized d-electrons. Rare-earth ortho-coaltites, LnCoO$_3$, where the low- and high-spin ions can coexist, localized as well as itinerant d-electron behaviour is observed depending on the experimental conditions.

Compounds of the general formula Ln$_{1-x}$Sr$_x$CoO$_3$ exhibit itinerant electron behaviour when $x > 0.15$ and compositions with $x > 0.40$ are generally metallic and ferromagnetic. Thus, by suitable variations in the proportions of the Ln, M or B ions one can significantly alter the electrical and chemical properties of these oxides.

Obayashi et al. have recently shown that LaNiO$_3$ and similar compounds of the type (Ln, M)BO$_3$ can be used as good ethanol sensors. In the presence of alcohol and air and at elevated temperatures, electrical resistivity of these oxides increases by amounts proportional to the percentage of ethanol present. Vrieland has observed that in the oxidation of ammonia over La$_{1-x}$Ca$_x$MnO$_3$, the Mn$^{3+}$ or Mn$^{4+}$ ions that are present, do not act as individual surface ions but rather as groups of ions, thus indicating that collective properties may be important. On the other hand, Voorhoeve et al. have related catalytic activity to the ease of forming anion vacancies during the reduction of CO and NO by hydrogen.

We have recently studied the electrical and magnetic properties of a series of compounds such as LaCo$_{1-x}$Ni$_x$O$_3$ and LaCo$_{1-x}$Fe$_x$O$_3$. On substitution of Ni for Co in LaCoO$_3$, electrical resistivity decreases and for $x > 0.5$ the system becomes metallic. Substitution of Fe for Co, on the other hand, increases the resistivity. These oxides seemed to be interesting systems for the investigation of catalytic activity since LaCoO$_3$ is a fairly good oxidation catalyst. We have, therefore, examined the oxidation of ethanol on these oxides and also followed the changes in electrical properties during the oxidation reaction. In addition, we have also examined the catalytic activity of two oxides of K$_2$NiF$_4$ structure, La$_4$NiO$_4$ and La$_2$CuO$_4$.

**Materials and Methods**

LaCo$_{1-x}$Ni$_x$O$_3$ and LaCo$_{1-x}$Fe$_x$O$_3$ were prepared from the mixed oxalates according to the procedure published earlier. La$_4$NiO$_4$ and La$_2$CuO$_4$ were also prepared from the mixed oxalates. The oxides from which the oxalates were prepared were all 99.9% pure. When used in powder form as catalyst all these compounds had comparable surface area of the order of 1-2 m$^2$/g.

Catalytic studies were carried out in glass reactors. Catalysts were kept in a static bed (1 g of powdered catalyst was used) and were covered with glass beads to ensure pre-heating of the reacting vapours to the catalyst-bed temperature. A chromel-alumel thermocouple, suitably protected against contact with the reactant vapours, was used to measure and control the temperature of the catalyst bed.

Ethanol-oxygen mixtures were passed over the catalyst. The reactant oxygen gas was also used as the carrier gas. Thoroughly dried oxygen gas was saturated with dry ethanol vapours by bubbling the oxygen thorough absolute ethanol chambers kept at 20° and the oxygen stream saturated with ethanol was passed over the catalyst. This ethanol-oxygen mixture will be referred to henceforth as the reaction mixture. The flow-rate used in our experiments was five litres of oxygen per hour per g of catalyst. The catalytic reactor was flushed with oxygen for 2 hr before the reaction mixture was introduced. After the reaction mixture was passed over the catalyst bed, it was analysed for carbon dioxide by absorbing in KOH solution and for other organic compounds by gas chromatography.

Reaction of ethanol with oxygen over the various catalysts is highly exothermic and it is difficult to
control the temperature of the catalyst bed at high conversions. The steady state temperature of the catalyst is stable over several days but is extremely sensitive to changes in the flow rate and the partial pressure of the reactants. Carbon dioxide was found to be the only product of oxidation of ethanol over the various catalysts studied. The extent of conversion depended on the temperature of the catalyst bed, the flow-rate of the reaction mixture, as well as the partial pressure of the reactants.

Electrical resistivity studies were carried out using pellets of the compound which were sintered at 850°. The pellets were 12 mm in diameter and 4 to 5 mm in height. The four-probe method (Pt probes) was used to measure the conductivity, corrections being made for changes in the dimensions of the pellets. The four-probe apparatus was enclosed in a glass tube and the inlet gas was introduced into the tube through a nozzle just over the pellet. Oxygen was passed over the sample for 2 hr to remove air from the glass tube before the reaction mixture was introduced. In the studies when ethanol-nitrogen mixture was used, the four-probe apparatus was initially flushed with nitrogen for 2 hr.

Results and Discussion

Results of our studies on the oxidation of ethanol over various LaCo₁₋₅Ni₄O₃ catalysts are given in Fig. 1 in which the percentage reaction of ethanol to give CO₂ is plotted against the reaction temperature. The activity of pure LaNiO₃ was very small even up to 240°. Obayashi et al. have reported that under the conditions employed by them (~100 ppm of ethanol in oxygen) there was 100% conversion of ethanol even at 230°. The high conversion obtained by them may be due to the very small amount of ethanol in their reaction stream.

As seen from Fig. 1 the cobalt substituted nickelites were generally more active than pure LaNiO₃. Fresh LaCoO₃ was very active, but this compound gets rapidly poisoned at high conversions and does not behave as a true catalyst. The change in activity of LaCo₁₋₅Ni₄O₃ compounds with increasing Co concentration is not very large. This small change in catalytic activity on cobalt substitution is to be contrasted with the large changes in the electrical and magnetic properties of these compounds as reported by Rao et al.

In Fig. 2 we have shown the activity of LaCo₁₋₅Fe₃O₄ as well as those of La₃NiO₄ and La₄CuO₄ for the formation of CO₂ during the oxidation of ethanol. Amongst the iron-substituted compounds, the composition with x = 0.01 is the most active, being more active than pure LaCoO₃ itself. This is interesting as further addition of iron reduces the activity. This discrepancy may be accounted for by the fact that the activity of pure LaCoO₃ for several catalysed reactions is dependent on the method of its preparation. This may be due to the slight deviations from the stoichiometry in the pure compounds while for doped samples there is a constancy in composition. In the case of the LaCo₁₋₅Fe₃O₄ compounds, changes in catalytic activity with x is paralleled by the changes in their electrical properties. Increase in conductivity is generally accompanied by increase in activity. However, La₃NiO₄ and La₄CuO₄ which have quite high conductivity are inactive towards the oxidation of ethanol. It seems, therefore, that individual ionic species are more important than the collective property in determining the catalytic activity of these oxides. In particular, it would seem that low-spin states are essential for reducing the activation energy for the oxygen transfer reaction. In the LaCo₁₋₅Ni₄O₃ compounds both the cobalt and nickel ions may exist in the low-spin states, so that even though cobalt substitution may change greatly the bulk electrical properties, the catalytic activity is not much affected. In the LaCo₁₋₅Fe₃O₄ compounds the iron ions can exist only in the high-spin state so that increasing iron substitution decreases the concentration of low-spin ions and hence the activity. These results are in agreement with earlier studies on the oxidation of CO over LnCoO₃ catalysts which required both low- and high-spin ions. The high-spin ions which are screened less by its outer electrons act as active.
centres for the adsorption of alcohol molecules while the low-spin ions are involved in the oxygen transfer process of surface oxygen ions to the alcohol molecule.

Changes in electrical properties — Since the spin-configuration of the $\text{Co}^{3+}$ or $\text{Ni}^{3+}$ ions in $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ determine the electrical properties of these compounds it was thought that a better insight into the mechanism of oxidation could be obtained by studying the electrical resistivity changes of these compounds in the presence of the reaction mixture.

In Figs. 3 and 4 are shown typical increase in resistivity that is observed for the $x = 0.75$ (a metal) and $x = 0.2$ (a semiconductor). In both these cases there is an increase in the resistance of the sample in the presence of the reaction mixture to a steady value, the time taken for reaching the steady value corresponding roughly with the time taken for the adsorption of the ethanol on the surface to be complete. The increase in resistivity in both cases rules out the possibility that it may be due to any local heating of the surface due to the exothermic nature of the reaction. Moreover, in the case of the metallic samples, the resistivity increase was much too high for it to be due to any heating that might be taking place. In the case of pure $\text{LaCoO}_3$ ($x = 0$) or those compounds in which $x$ is very small ($x < 0.1$) there is an increase in the electrical resistivity in the presence of the reaction mixture, but only at low temperatures where there is practically no conversion. At higher temperatures when there is considerable oxidation and hence considerable evolution of heat the resistivity decreases on the introduction of the reaction mixture. This is understandable for when $x$ is small the compounds are semiconductors with rather high activation energies and hence the thermal effect should be considerable.

Obayashi et al. have listed various mechanisms to account for the increase in resistivity: (i) narrowing of bands due to the creation of anion vacancies which decrease the strength of the metal-oxygen-metal interactions; (ii) creation of additional scattering centres; and (iii) change in the spin-state of metal ions. It is difficult to identify the exact reason for the change in resistivity, but change in the spin-state of the ion implies changes in the band-width and also changes in the number of scattering centres. In line with our findings on the relation of catalytic activity to presence of high- or low-spin ions, we attribute the changes in the resistivity to the changes in the spin state of the metal ions.

It has been shown by Rao et al. that the presence of high-spin ions in the $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$ compounds increases the resistivity of these compounds. The increase in the resistance of these compounds in the presence of the reaction mixture could therefore be due to the conversion of a low-spin ion to a high-spin ion. In $\text{LaCoO}_3$ there is an equilibrium between high- and low-spin ions due to the crystal-field splitting, $\Delta_{\text{ef}}$, being nearly equal to the exchange energy, $\Delta_{\text{ex}}$. Thus, in the cobalt-rich compounds any factor that decreases the crystal-field splitting would increase the concentration of high-spin ions. In the present
case the crystal-field strength may be reduced by the adsorption of an alcohol molecule on an oxide ion. In the case of the nickel-rich compounds of the type \( \text{LaCo}_{1-x} \text{Ni}_x \text{O}_3 \) \((x \approx 1)\) there is a reversible loss of oxygen from these compounds in the temperature range in which these compounds become active as catalysts for the oxidation reaction. This was first demonstrated in the case of pure \( \text{LaNiO}_3 \) by Gai and Rao. At low temperatures when there is no oxygen loss from the catalyst it may be assumed that high-spin \( \text{Ni}^{3+} \) ions are formed on the adsorption of alcohol. These high-spin ions would be the intermediate in the conversion of the low-spin \( \text{Ni}^{3+} \) ions to the high-spin \( \text{Ni}^{2+} \) state on the loss of oxygen. The above model involving the formation of high-spin ions on the adsorption of alcohol would account for the exchanges in resistivity in the presence of the reaction mixture at various temperatures.

In Fig. 5, curve A gives the percentage increase in resistivity at saturation at various temperatures for the \( x = 0.75 \) compound. These values are taken from Fig. 3. As seen from Fig. 5 the curve has a maximum at a temperature corresponding to a rapid increase in the rate of oxidation. A similar curve is obtained if the catalyst is heated in the presence of the reaction mixture (see for instance the inset of Fig. 4 and curve C of Fig. 5). In curve B (Fig. 5) the \( \text{LaCo}_{0.75} \text{Ni}_{0.25} \text{O}_3 \) compound was exposed to the reaction mixture for two hours at 140° and then kept overnight at the same temperature in oxygen alone. The alcohol from the gas-phase was removed by flushing with nitrogen, and the surface contained only irreversibly adsorbed alcohol molecules or some intermediate. As seen from the Fig. 5 when the temperature is increased at the rate of 1°/min the resistivity increases rather sharply. Above 200° when the rate of oxidation is relatively high, the resistivity decreases very rapidly to the original value of the compound in the presence of pure oxygen.

Two factors seem to be involved which account for the changes observed in curve B (Fig. 5). The first factor involves the strength of the interaction of the adsorbate with the surface which would increase with temperature. By the mechanism proposed earlier the number of high-spin ions would therefore increase with temperature and hence the resistivity also. The second factor is the number of strongly adsorbed molecules on the surface. Above 200° the number of such molecules on the surface and hence the resistivity would decrease due to the high rate of oxidation. The maxima that occurs in curves of the type A in Fig. 5 for the various compounds then depend on the strength of the interaction of the alcohol molecule with the surface and the rate of its oxidation at various temperatures. Obayashi et al. have stated that the resistivity change that is observed in the presence of the reaction mixture could not be due to the adsorption of alcohol molecules, as at low temperatures, the weight of alcohol adsorbed decreases with increasing temperature while the resistivity increases. This overlooks the fact that only strongly adsorbed alcohol molecules may be responsible for the increase in resistivity. The number of such molecules is usually far less than the total number of alcohol molecules adsorbed on the surface.

In the presence of alcohol-nitrogen mixtures the increase in resistivity at low temperatures is similar to that in the presence of alcohol-oxygen mixture. When a compound is heated slowly in the presence of alcohol-nitrogen mixtures the resistivity change shows a maximum at a temperature corresponding to that in the presence of alcohol-oxygen mixture. The maximum is followed by a shallow minimum after which the resistivity increases again with temperature. The maximum is obviously due to the desorption of some of the alcohol molecules adsorbed on the surface. The increase in resistivity at higher temperatures is due to the creation of anion vacancies.

When alcohol was passed along with nitrogen at 350° (100% oxidation takes place at this temperature) over various compounds there was a steady decrease in the weight of the compound showing the creation of anion vacancies. Simultaneously the resistivity of the sample also increased. On the introduction of oxygen the weight lost was recovered very quickly (<5 min) and the resistivity decreased to its original value simultaneously. This shows that the activity for oxidation arises out of the ability of the compound to react with the alcohol molecule and the rapid replenishment of the surface oxygen consumed in the oxidation process.

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References

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