

# Carbon Monoxide Oxidation on Nickel Chromite

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The kinetics of the oxidation of carbon monoxide has been studied with a stoichiometric mixture of CO and O<sub>2</sub> at an initial pressure of 50 torr and in the temperature range 180-230°. The rate of the reaction depends only on oxygen partial pressure. *In situ* electrical conductivity and adsorption studies have been carried out to explain the break in kinetic plots. The compound nickel chromite has been found to be more active than the component oxides and this may be due to the synergetic effect usually observed in the case of spinels.

MANY oxide catalysts like CuCr<sub>2</sub>O<sub>4</sub>, LaCoO<sub>3</sub>, etc., have become potential substitutes for the costly noble metal catalysts in the catalytic reactors used in control of automotive emissions. To optimize catalytic performance of these catalysts, a knowledge of the mechanism and the kinetics of the reaction is required. Carbon monoxide is the major pollutant of automotive emissions. In an attempt to contribute to the wealth of literature on the oxidation of carbon monoxide, we have chosen the chromites of transition metals with the general formula MCr<sub>2</sub>O<sub>4</sub> (where M is a divalent transition metal ion like Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, etc.) as catalysts for the study. Though these chromites have been tested for their activity for CO oxidation<sup>1</sup>, no systematic study has been made to compare the activity and stability of these catalysts. In this paper the work on the spinel nickel chromite has been reported.

## Materials and Methods

NiCr<sub>2</sub>O<sub>4</sub> has been prepared by firing the co-precipitated hydroxides (at pH 6) of nickel and chromium at 950° for 30 hr. The formation of single spinel phase was checked by X-ray method. The component oxides have also been prepared from their respective hydroxides in a similar way.

The kinetics of the reaction  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$  has been studied following the pressure change with time in a static reactor with a recirculation pump. The gases, oxygen and carbon dioxide, from cylinders (Indian Oxygen Limited), were purified in the usual way. Pure carbon monoxide was prepared by the method of Weinhouse<sup>2</sup>.

The surface of the catalyst was purified by continuously evacuating the catalyst at a pressure of 10<sup>-6</sup> torr at 400° for 6 hr. The catalyst was then soaked in 100 torr of oxygen at the reaction temperature for nearly 10 hr. Before the reaction, the physically adsorbed molecules were removed by pumping for 2-3 min. This kind of treatment of the catalyst was found to give good reproducibility.

The surface area of the catalyst as measured by the BET (N<sub>2</sub>) method was found to be 7.8 m<sup>2</sup>/g.

Electrical conductivity measurements *in situ* have been done using a two-probe cell. Adsorption measurements have been carried out in a volumetric set-up.

## Results and Discussion

The kinetics of oxidation of CO by oxygen was studied at an initial total pressure of 50 torr of a mixture of CO and O<sub>2</sub> in the ratio 2:1 in the temperature range 180-230°. The total order of the reaction and the order with respect to oxygen partial pressure were found to be the same, viz. 0.5, by varying the pressures over a wide range. The rate was, however, found to be independent of CO partial pressure. The product CO<sub>2</sub> does not inhibit the reaction.

CO adsorption experiments have been tried in the temperature range 25-100° as above this temperature CO might start reacting with the surface though in small amounts. The results showed the failure of CO to get adsorbed on the surface. CO<sub>2</sub> did not adsorb on the surface, even at reaction temperatures.

Oxygen adsorption was found to be extremely small in the reaction temperature range. A three-fold decrease in resistance observed when oxygen was admitted to a freshly evacuated catalyst confirmed adsorption of oxygen on the surface (Fig. 1).

The kinetic data were analysed using the rate equations (1) and (2)

$$\text{Rate} = k' P_{\text{O}_2}^{\frac{1}{2}} \quad \dots(1)$$

$$\text{Rate} = \frac{k P_{\text{O}_2}^{\frac{1}{2}}}{1 + b P_{\text{O}_2}^{\frac{1}{2}}} \quad \dots(2)$$

where  $k$  and  $k'$  are the rate constants and  $b$  is the adsorption coefficient. Eq. (2) was found to give a better fit for the kinetic data obtained.

The plots of 1/rate versus  $1/P_{\text{O}_2}^{\frac{1}{2}}$  at 182° and 196° show distinct breaks (Fig. 2) when the conversion is around 10%. In order to get a possible insight into what really happens at and after the break

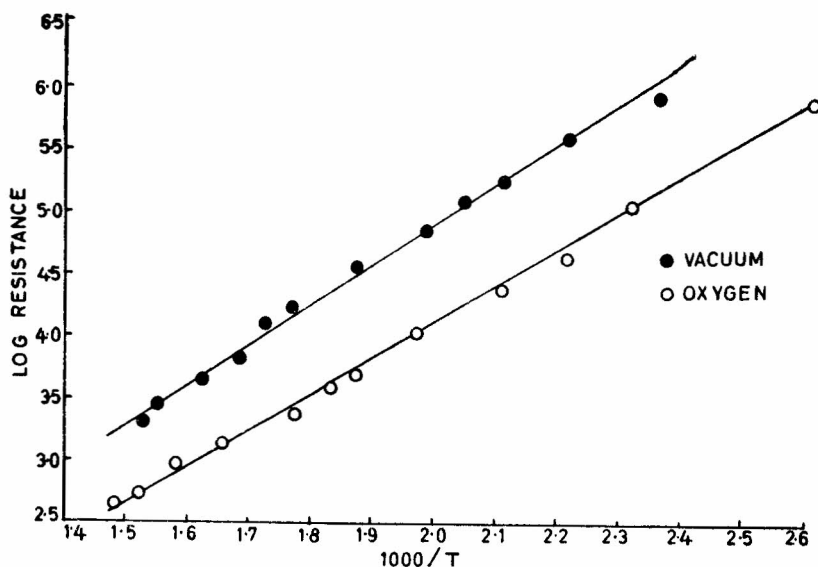


Fig. 1 — Arrhenius plots for electrical conduction

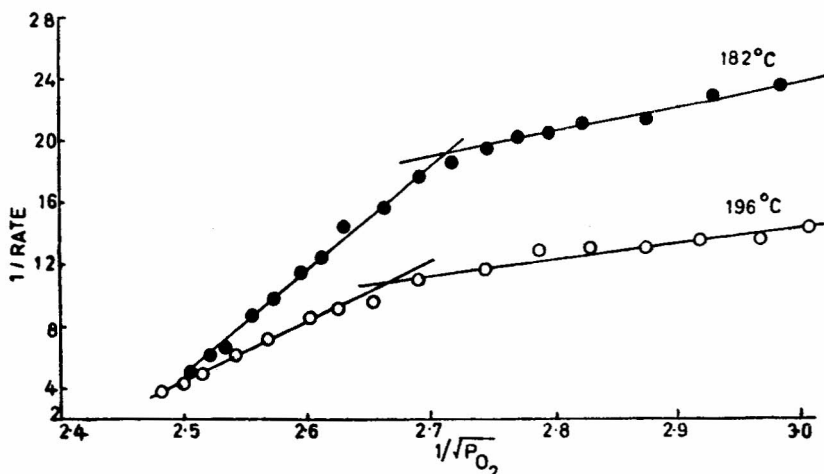


Fig. 2 — Kinetic plots for the oxidation of CO

point, *in situ* conductivity studies have been made and the results are discussed below.

Admission of pure CO on the freshly evacuated catalyst in the reaction temperature range did not result in any conductivity change thus indicating the absence of simple reduction-oxidation mechanism for the reaction. In this connection it may be mentioned that Cr<sup>3+</sup> usually imparts stability to the catalyst. It has been observed by Rennard *et al.*<sup>3</sup> that the reduction of MgCr<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> catalyst becomes difficult as 'x' tends to 2.

When pure CO was admitted over an oxygen pretreated catalyst from which oxygen has been pumped out for 2 min., a very small change in conductivity was observed. However, when a mixture of CO and O<sub>2</sub> in the ratio 2:1 was admitted over the same catalyst, conductivity change could be followed for a longer time though the change becomes small with time. All these observations indicate that oxygen gas is essential for the oxidation of CO on NiCr<sub>2</sub>O<sub>4</sub>.

In order to check whether the break point in the kinetic plot disappears by taking a gaseous mixture of CO, O<sub>2</sub> and CO<sub>2</sub> with a composition corresponding to a point after the break, kinetics has been followed with a mixture of CO, O<sub>2</sub> and CO<sub>2</sub> in the ratio 4:2:1. Rate Eq. (2) was used in this case also and the kinetic plots are shown in Fig. 3. As expected there was no break in the kinetic plots. However, the activation energy for the reaction (16.0 kcal mole<sup>-1</sup>) in this case (total pressure 50 torr) is nearly equivalent to the activation energy value (14.9 kcal mole<sup>-1</sup>) before the break point in the case of reaction (total pressure 50 torr) with stoichiometric amounts of CO and O<sub>2</sub>. This may simply mean that the situation before break point in the case of stoichiometric mixture is the same as that achieved when CO, O<sub>2</sub> and CO<sub>2</sub> is taken in the ratio 4:2:1. Since neither CO nor CO<sub>2</sub> gets adsorbed on the surface, it is quite possible that all the observations reported above have to be attributed only to some change in the nature of oxygen species.

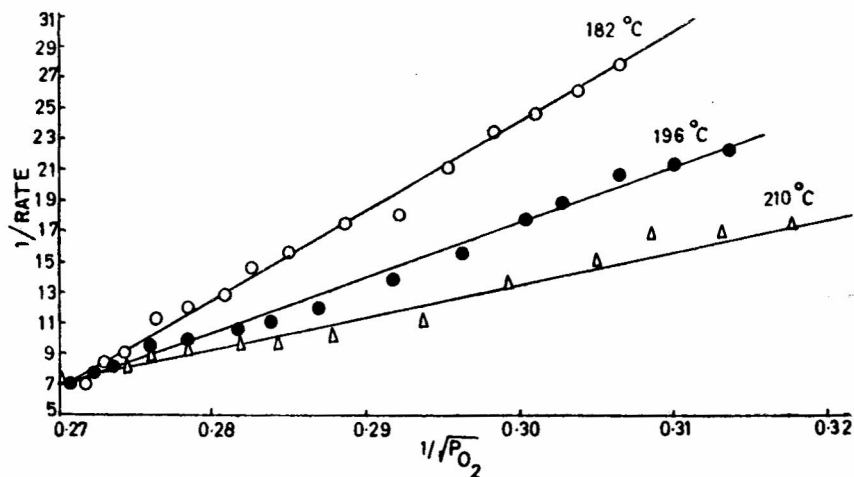
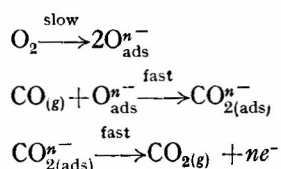


Fig. 3 — Kinetic plots for the oxidation of a mixture containing CO, O<sub>2</sub> and CO<sub>2</sub> in the ratio 4:2:1

Initial ESR experiments showed the absence of the formation of paramagnetic O<sub>2</sub><sup>-</sup> on the surface. Further studies are in progress to identify the species.

The overall mechanism of the reaction may therefore be written as follows:



The kinetics of the oxidation on NiO (surface area=1.5 m<sup>2</sup>/g) could not be followed below 350°. It is well known that the activity of NiO can be very much varied by changing the method and temperature of preparation<sup>4</sup>. The surface area of NiO has been reported<sup>4</sup> to fall from 30.5 to 2 m<sup>2</sup>/g when the temperature of preparation has been raised from 500° to 900°. In the case of chromia, the reaction could be followed only above 290°. It is also known that the activity of chromia for CO oxidation and its surface area do not depend very much on the temperature of preparation<sup>5</sup>. The mechanism of CO oxidation on these two oxides is also known to be different from that on nickel chromite<sup>6,7</sup>. In order to have a meaningful comparison of the activities of these oxides one has, therefore, to choose either the percentage conversion

in a fixed period at a common temperature or the temperature at which a particular conversion is obtained during a fixed period as a measure of the activity of the catalyst. In this paper the latter has been chosen since the temperature at which these oxides have been found to be active are quite different. Further the temperature of preparation of the catalysts was kept the same in all cases in order to ensure that the effect of this parameter is eliminated. It has been found that nickel chromite is more active than the component oxides. This could be due to the synergetic effect usually observed in the case of spinel compounds.

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