

CATALYTIC OXIDATION OF CARBON MONOXIDE ON SPINEL TYPE FERRITES — ROLE OF MAGNETIC EXCHANGE INTERACTIONS

by K. R. KRISHNAMURTHY*, B. VISWANATHAN and M. V. C. SASTRI**, F.N.A.,
Department of Chemistry, Indian Institute of Technology, Madras-600036

(Received 1 March 1976; after revision 17 August 1976)

The catalytic oxidation of CO has been studied on a series of spinel type ferrites MFe_2O_4 (M is Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) and on $Ni_xZn_{1-x}Fe_2O_4$ mixed ferrites. From the consideration of activity, cation distribution and saturation magnetization, it is shown that the adsorption of CO as a positive species, which is the rate determining step in the overall mechanism of the reaction, is facilitated in those systems which possess magnetic ordering brought out by exchange interactions between the cations at the two crystal field environments.

INTRODUCTION

Some attempts have been made in recent years to relate the catalytic properties of spinel type ferrites with their characteristic magnetic properties. Thus Forestier and Lille (1937) observed that the activities of Fe_3O_4 , $SrFe_2O_4$ and $NiFe_2O_4$ in the water gas shift reaction ($CO_2 + H_2 = CO + H_2O$) increased sharply at their respective Curie temperatures. More recently, Wolski (1962) studied the oxidation of formic acid by hydrogen peroxide in presence of mixed Ni-Zn mixed ferrites ($Ni_xZn_{1-x}Fe_2O_4$, where $0 < x < 1$, x denoting the fraction of a gram-atom present in the gram-molecular weight of the compound) and noted a quantitative relationship between saturation magnetic moment and catalytic activity. In the present work, this relationship is examined in depth with respect to the activity of ferrites in a different type of reaction, namely, the oxidation of carbon monoxide by oxygen. Unlike the other reactions so far studied in this context, it has been shown, as a matter of special interest, to involve the participation of the lattice oxygen atoms in the actual surface process.

EXPERIMENTAL

The ferrite catalysts were prepared by co-precipitation technique and subjected to chemical analysis, X-ray, far-IR and electrical and magnetic characterizations by Faraday balance and the cation distributions were computed from the intensities of the X-ray diffraction lines.

The catalytic activities of the ferrites for the oxidation of carbon monoxide (expressed in terms of the first order rate constants, $\text{min}^{-1}\text{m}^{-2}$) were evaluated employing a static reactor provided with an electromagnetically operated all-glass

**Present Address* : Research Chemist, Indian Petrochemicals Corpn. Ltd., Jawaharnagar, Baroda-391320.

***Present Address* : Head, Materials Science Research Centre, Indian Institute of Technology, Madras-600036.

pump for circulating the reaction mixture over the catalyst. The rate of the reaction was followed by admitting a stoichiometric mixture of CO and O₂ + diluent, if any, to the system to give an initial total pressure of 70±1 torr, noting the decline of pressure as a function of time and applying the stoichiometric equation to evaluate $-dP_{CO}/dt$. Where necessary, the increase in CO₂ concentration was determined by gas chromatography. The weight of the catalyst placed in the reactor varied from 1.5 to 2 g.

The kinetics were studied in the temperature range 420–480°C for Mn-ferrite, 150–170°C for magnetite, 200–280°C for CO-ferrite, 230–260°C for Ni-ferrite, 205–245°C for Cu-ferrite and 280–320°C for Zn-ferrite. Prior to each run, the catalysts were activated by evacuation at 10⁻⁵ torr at 400°C for 6 hours and pretreated with oxygen at a pressure of about 100 torr for 10 hours at the reaction temperature. This procedure was found to give reproducible kinetic data.

RESULTS AND DISCUSSION

From the results of their studies on the oxidation of CO by spinel ferrites, Schwab *et al.* (1953) concluded that (i) Fe³⁺ ions present at the octahedral sites alone were active, (ii) the normal ferrites were more active than the inverse ferrites, and (iii) the nature of the divalent ion had no bearing on the catalytic activity. These conclusions are subjected to critical scrutiny in the present work.

All the data relative to the simple ferrites are presented in Table I. It is seen that, with the exception of Cu and Zn ferrites, the catalytic oxidation activities of the simple ferrites increase in the same order as their saturation magnetizations. The correlation between the two properties is more evident in the case of Ni-Zn mixed ferrites. Fig. 1 (Plots A & B) shows the striking similarity between the trends of variation of both these properties with the Ni/Zn ratio, with both exhibiting maxima at Ni/Zn = 1.

TABLE I
Catalytic activity, cation distribution and saturation magnetisation of simple ferrites

| Ferrite | Cation distribution | | Saturation magnetisation in CGS units at 300 k (k in min ⁻¹ m ⁻²) | Catalytic activity |
|----------------------------------|---|---|--|-------------------------|
| | A Site | B Site | | |
| Fe ₃ O ₄ | Fe ³⁺ | Fe ²⁺ Fe ³⁺ | 87.0 | 11.9 × 10 ⁻⁴ |
| MnFe ₂ O ₄ | Mn _{0.8} ²⁺ Fe _{0.2} ³⁺ | Mn _{0.2} ²⁺ Fe _{1.8} ³⁺ | 80.0 | 6.20 × 10 ⁻⁴ |
| CoFe ₂ O ₄ | Fe ³⁺ | Fe ³⁺ CO ²⁺ | 78.0 | 3.20 × 10 ⁻⁴ |
| NiFe ₂ O ₄ | Fe ³⁺ | Ni ²⁺ Fe ³⁺ | 50.0 | 2.60 × 10 ⁻⁴ |
| CuFe ₂ O ₄ | Cu _{0.04} Fe _{0.96} ³⁺ | Cu _{0.96} ²⁺ Fe _{1.04} ³⁺ | 26.4 | 39.0 × 10 ⁻⁴ |
| ZnFe ₂ O ₄ | Zn ²⁺ | 2Fe ³⁺ | 0 | 3.60 × 10 ⁻⁴ |

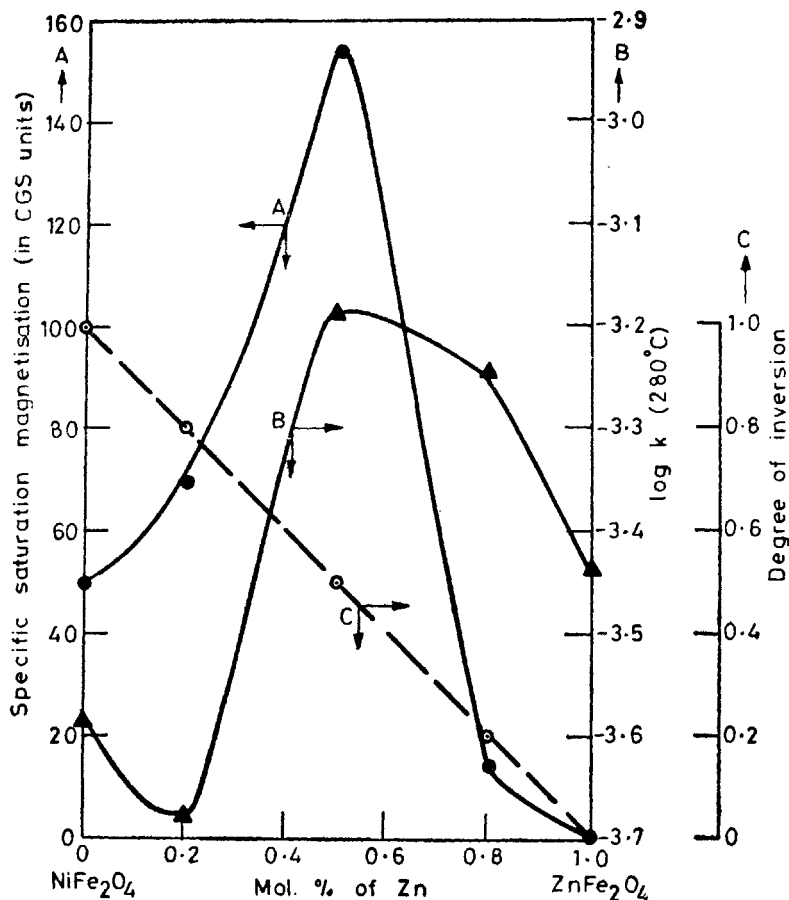


FIG. 1

The activities of the simple ferrites follow the order $\text{CuFe}_2\text{O}_4 > \text{Fe}_3\text{O}_4 > \text{MnFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4$. That is, contrary to Schwab *et al.* (*loc. cit.*), the inverse ferrites, CuFe_2O_4 and Fe_3O_4 , are more active than the normal ferrite, ZnFe_2O_4 . The lack of correlation between the degree of inversion (or cation distribution) and catalytic activity is brought out strikingly in the case of the Ni-Zn ferrites by comparing plots B and C of Fig. 1. The composition, $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, manifests the maximum activity, those more 'normal' or more "inverse" than this being less active. It is clear, therefore, that the Fe^{3+} ions at the octahedral sites and those at the tetrahedral ones are both held responsible for the catalytic activity of the ferrites though the former may be the major active species. The striking similarities between the variation of saturation magnetization values and activity in the case of both simple and mixed ferrites show that the nature of the divalent ions has a decisive role in controlling the activity.

The ferrimagnetic behaviour of spinel-ferrites is governed by the distribution of cations among the octahedral (B) and tetrahedral (A) sites in the structure and the exchange interaction between the ions in different sites (Smit & Wijn 1959).

The ferrites MnFe_2O_4 , FeFe_2O_4 , CoFe_2O_4 , NiFe_2O_4 and CuFe_2O_4 have almost complete inverse spinel structure, *i.e.*, the divalent ions are present at the octahedral (B) sites while the ferric ions are equally distributed between the octahedral (B) and tetrahedral (A) sites, with the result that the saturation magnetization, M_s , corresponds to the spin of 'A' ions only. The M_s values for the ferrite spinels vary in the following order :

$$\begin{array}{cccccc}
 \text{CuFe}_2\text{O}_4 < \text{NiFe}_2\text{O}_4 < \text{CoFe}_2\text{O}_4 < \text{FeFe}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 \\
 M_s(\mu_B) & 1.3 & 2.2 & 3.7 & 4.1 & 4.6
 \end{array}$$

This trend is similar (but in reverse order) to the activity pattern observed for the oxidation of CO, with the exception of CuFe_2O_4 , showing that the activity is dependent upon the exchange interactions between the cations at the two different crystal field environments.

In the oxidation of carbon monoxide it has been shown (Krishnamurthy 1975) that the adsorption of CO as a positive species is the rate controlling step. It is probable that this charge transfer is facilitated in these systems because of the magnetic ordering at the octahedral sites brought about by the presence of a certain minimum amount of magnetic ions at the tetrahedral sites (say, Fe^{3+} or M^{2+}). In this sense, the ions at the tetrahedral sites can be expected to influence the activity. This conclusion is supported by the observation that activity and saturation magnetization show similar trends of variation with composition in the case of Ni-Zn mixed ferrites.

However, the lower activity of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ relative to that of NiFe_2O_4 , appears to be anomalous in this context. It is of interest to note in this connection that from measurements of the electrical conductivity of the Ni-Zn ferrites, it has been found that the activation energy for electrical conduction registers a maximum at this composition, which correlates with the dip in catalytic activity. This indicates that at such low concentrations of Zn the electronic factors prevail over the magnetic interaction effects. The former, which plays an important role in the mechanism of the catalytic oxidation of carbon monoxide on oxide surfaces, will be discussed more fully in another paper.

Finally, the high activity of Cu ferrites arises presumably from (i) the Cu^{2+} ions present in octahedral sites experiencing a Jahn-Teller distortion, and (ii) the high mobility of the charge carriers as evidenced by the low value of the activation energy (E_σ) for electrical conduction.

ACKNOWLEDGEMENT

Fund-support provided by the Department of Science and Technology and the award of a C.S.I.R. Research Fellowship to K.R.K. are gratefully acknowledged.

REFERENCES

- Forestier, H., and Lille, R. (1937). Variation in catalytic process of ferromagnetic substances at Curie point. *C.r. Acad. Sci., Paris* **204**, 1254.

- Krishnamurthy, K. R. (1975). Studies on the catalytic oxidation of carbon monoxide on spinel type ferrites. *Ph. D. Thesis*, Indian Institute of Technology, Madras.
- Schwab, G. M., Roth, E., Grintzos, Ch., and Mavrakis, N. (1953). *Structure and Properties of Solid Surfaces*. University of Chicago Press, Chicago, pp. 464.
- Smit, J., and Wijn, H. P. J. (1959). *Ferrites*. Philips Technical Library, Eindhoven.
- Wolski, W. (1962). Magnetic and catalytic properties of Ni-Zn ferrites. *Russ. J. inorg. Chem.*, **7**, 922.