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CATALYTIC ACTIVITY OF TRANSITION METAL  
SPINEL TYPE FERRITES: STRUCTURE-ACTIVITY  
CORRELATIONS IN THE OXIDATION OF CO.

By

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In the spinel type ferrites of the formula  $MFe_2O_4$ , the divalent and the ferric ions can occupy octahedral and tetrahedral holes of the lattice<sup>1)</sup>. The possibility of the presence of metal ions in more than one geometrical environment leads to the surface heterogeneity. Besides the simultaneous presence of ferric ions in both octahedral and tetrahedral sites presents a means for evaluating the activity as a function of coordination geometry. The crystallographic environments of the metal ions often influence the resulting catalytic activity and the observed activity patterns have been examined by DOWDEN<sup>2)</sup> on the basis of crystal field theory.

SCHWAB *et al.*<sup>3)</sup> have observed that the normal ferrites are more active than inverse ferrites for the oxidation of CO and that the divalent metal ions do not play any role in the resultant activity. On the other hand, BORESKOV *et al.*<sup>4)</sup> have reported that the inverse ferrites like  $CoFe_2O_4$ ,  $NiFe_2O_4$  and  $CuFe_2O_4$  are more active for the oxidation of methane and hydrogen than the normal ferrites like  $ZnFe_2O_4$ . In the case of oxidative dehydrogenation of butenes, RENNARD and KHEL<sup>5)</sup> have shown that the inverse ferrite  $MgFe_2O_4$  is more active than the normal zinc ferrite. Between the two inverse ferrites  $CoFe_2O_4$  and  $CuFe_2O_4$ , the latter has been shown to be more active<sup>6)</sup>. From these studies, it appears that the relative activity of ferric ions at the two different crystallographic environments and the effect of the presence of divalent ions at these two types of sites of spinel lattice have not been established unequivocally.

In the present paper, results of a systematic study on the oxidation of CO on a number of spinel type ferrites of the general formula  $MFe_2O_4$  where M is

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TABLE 1. Physico-chemical properties of spinel type ferrites and the values of rate constants for the oxidation of CO

Ferrite	Unit cell parameter (A)	Activation energy for electrical conduction (eV)	Specific saturation magnetisation in CGS units.	Surface area (m <sup>2</sup> /g)	Cation distribution		Rate constant at 280°C (min <sup>-1</sup> m <sup>-2</sup> )
					A site	B site	
MnFe <sub>2</sub> O <sub>4</sub>	8.5	0.44 (<300°C) 0.56 (>300°C)	80.0	0.5	[Mn <sub>0.75</sub> <sup>2+</sup> Fe <sub>0.25</sub> <sup>3+</sup> ]	[Mn <sub>0.25</sub> <sup>2+</sup> Fe <sub>0.75</sub> <sup>3+</sup> ]	6.2 × 10 <sup>-4</sup>
Fe <sub>3</sub> O <sub>4</sub>	8.38	—	87.0	31.1	[Fe <sup>3+</sup> ]	[Fe <sup>2+</sup> +Fe <sup>3+</sup> ]	1.2 × 10 <sup>-3</sup>
CoFe <sub>2</sub> O <sub>4</sub>	8.381	0.57	78.0	7.5	[Fe <sup>3+</sup> ]	[Co <sup>2+</sup> +Fe <sup>3+</sup> ]	3.2 × 10 <sup>-4</sup>
NiFe <sub>2</sub> O <sub>4</sub>	8.305	0.49	50.0	7.7	[Fe <sup>3+</sup> ]	[Ni <sup>2+</sup> +Fe <sup>3+</sup> ]	2.6 × 10 <sup>-4</sup>
CuFe <sub>2</sub> O <sub>4</sub>	a = 8.2 c = 8.726	0.75 (360~450°C) 0.35 (200~360°C)	26.4	0.9	[Cu <sub>0.96</sub> <sup>2+</sup> Fe <sub>0.04</sub> <sup>3+</sup> ]	[Cu <sub>0.04</sub> <sup>2+</sup> Fe <sub>0.96</sub> <sup>3+</sup> ]	3.9 × 10 <sup>-3</sup>
ZnFe <sub>2</sub> O <sub>4</sub>	8.424	1.02	—	6.6	[Zn <sup>2+</sup> ]	[Fe <sub>2</sub> <sup>3+</sup> ]	3.6 × 10 <sup>-4</sup>
Zn <sub>0.8</sub> Ni <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	—	0.76	10.7	4.5	[Zn <sub>0.8</sub> <sup>2+</sup> Fe <sub>0.2</sub> <sup>3+</sup> ]	[Ni <sub>0.2</sub> <sup>2+</sup> Fe <sub>0.8</sub> <sup>3+</sup> ]	5.7 × 10 <sup>-4</sup>
Zn <sub>0.5</sub> Ni <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	—	0.46 (<280°C) 0.56 (>280°C)	153.7	2.3	[Zn <sub>0.5</sub> <sup>2+</sup> Fe <sub>0.5</sub> <sup>3+</sup> ]	[Ni <sub>0.5</sub> <sup>2+</sup> Fe <sub>0.5</sub> <sup>3+</sup> ]	6.5 × 10 <sup>-4</sup>
Zn <sub>0.2</sub> Ni <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	—	0.62 (<470°C) 1.1 (>470°C)	69.6	4.6	[Zn <sub>0.2</sub> <sup>2+</sup> Fe <sub>0.8</sub> <sup>3+</sup> ]	[Ni <sub>0.8</sub> <sup>2+</sup> Fe <sub>0.2</sub> <sup>3+</sup> ]	2.1 × 10 <sup>-4</sup>

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*Catalytic Activity of Transition Metal Spinel Type Ferrites*

$Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  and on a series of Ni-Zn mixed ferrites of composition  $Ni_xZn_{1-x}Fe_2O_4$  ( $0 < x < 1$ ) are presented with a view to

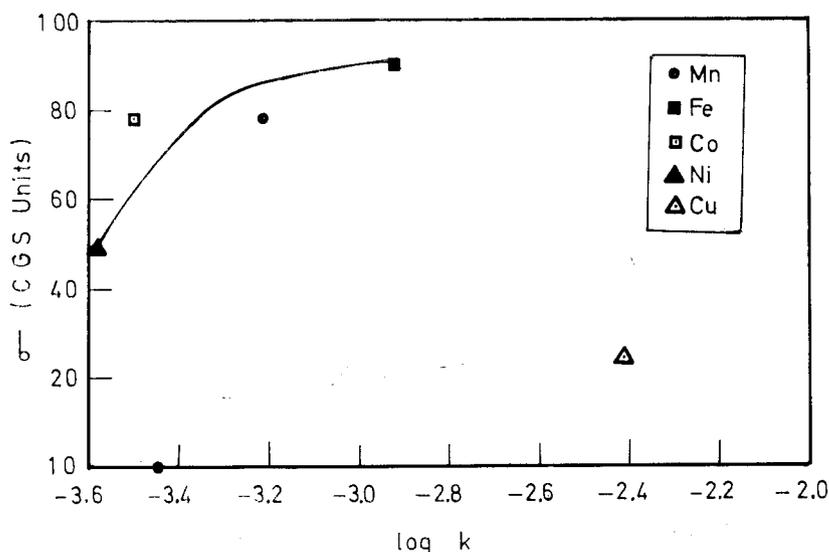
- a) unravel any correlations between structural parameters and other physical properties and the catalytic activity for rationalising catalyst selection<sup>7)</sup>,
- b) identify the active species and its coordination sphere, and
- c) evaluate the influence of cations present in octahedral and tetrahedral sites.

### Experimental

The catalysts (except  $MnFe_2O_4$  and  $Fe_3O_4$ ) were prepared by coprecipitation as hydroxides and calcination at  $650^\circ C$ . The ferrites obtained were characterised by chemical analysis, XRD studies, electrical conductivity, Seebeck coefficient, magnetic susceptibility and far IR spectroscopic measurements. The cation distributions were computed from the intensities of X-ray diffraction lines. The catalytic reaction studies were carried out in a static recirculatory reactor system<sup>8)</sup>.

### Results

The physico-chemical properties of the ferrite samples used in the present work are tabulated in Table 1. Detailed kinetic and mechanistic studies have been carried on the oxidation of CO on ferrites which form the subject matter of a separate communication<sup>9)</sup>. The important findings relevant to the subject



**Fig. 1.** Variation of activity with saturation magnetisation of simple ferrites.

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matter of the present paper are :

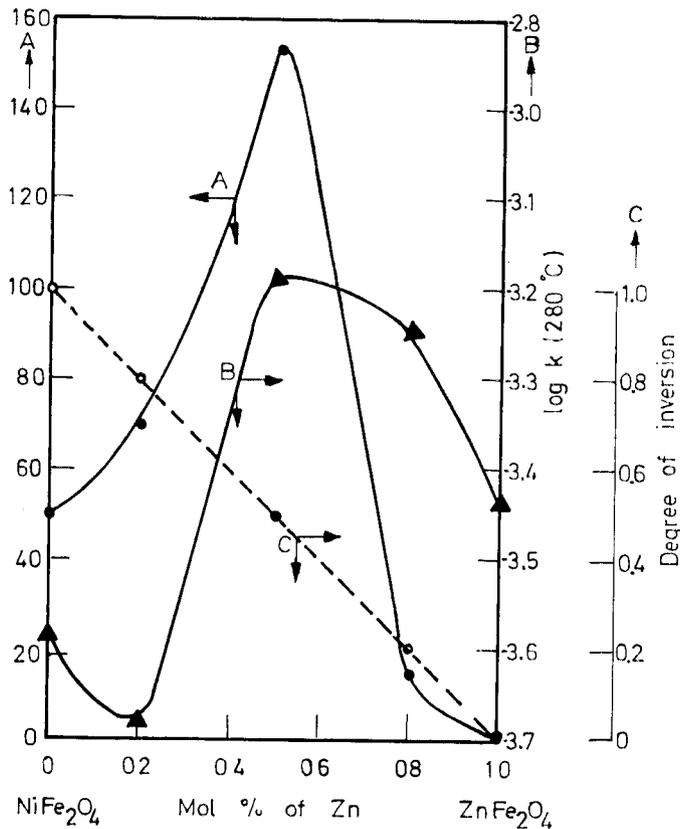
1) The reaction follows a rate equation which is first order with respect to the partial pressure of CO.

2) The adsorption of CO as a positively charged species is the rate controlling step in the overall mechanism of the reaction.

3) Various types of carbonate species (mono-and bi-dendate) are formed on the surface of the solid which decompose to give rise to  $\text{CO}_2$ .

4) Oxygen is chemisorbed in an ionic form ( $\text{O}_2^-$  or  $\text{O}^-$ ) but the reaction with CO proceeds through the participation of the lattice oxygen.

5) There is linear relationship between the values of apparent activation energy  $E_a$ , and the logarithm of the values of frequency factor denoting the presence of compensation effect. Therefore, in the present paper, activities are expressed in terms of the values of the rate constant (in  $\text{min}^{-1} \text{m}^{-2}$ ) at  $280^\circ\text{C}$ .



**Fig. 2.** Variation of activity and cation distribution of mixed ferrites as a function of composition.

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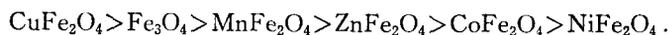
The correlations attempted include

a) the variation of activity of simple ferrites against their saturation magnetisation at 300°K (shown in Fig. 1),

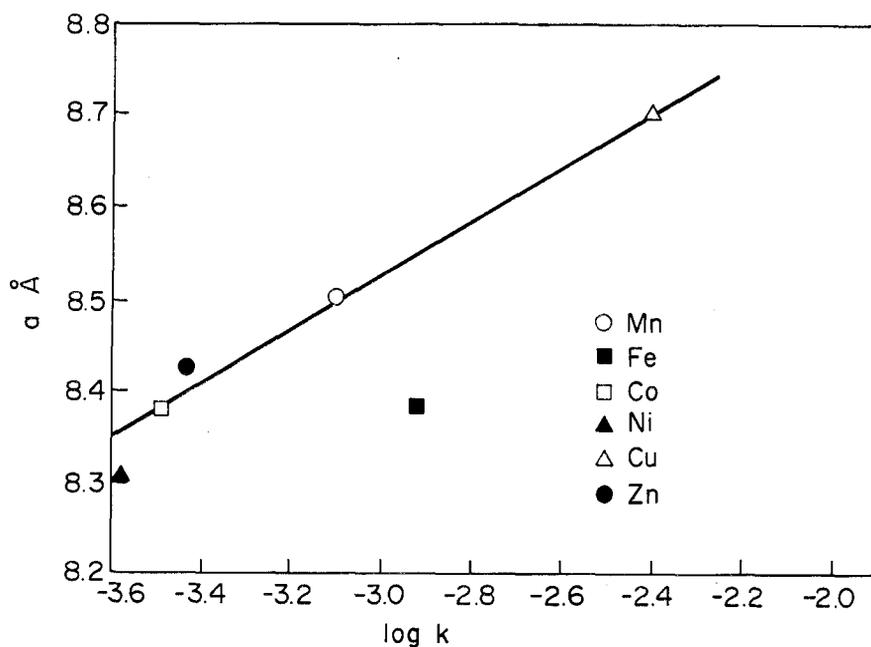
b) the relationship between the degree of inversion (cation distribution), activity and saturation magnetisation at 300°K (A) and the composition of the nickel-zinc mixed ferrites (Fig. 2), and

c) variation of activity with unit cell parameter, activation energy for electrical conductivity and surface oxygen bond energy are given in Figs. 3~5.

The gradation of activity for CO oxidation among the different ferrites investigated in the present work is



There appears to be no definite correlation between the degree of inversion (or cation distribution) and the catalytic activity as is evident from Fig. 2 where the degree of inversion increases linearly with the nickel content while the activity shows a maximum at the composition  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ . The maximum activity corresponds with the maximum value for saturation magnetisation at this composition which has to be rationalised on the basis of magnetic ordering of the octahedral cations (B sites) due to a AB interaction with the cations at the tet-



**Fig. 3.** Correlation between unit cell parameter and activity of simple ferrites.

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rahedral sites (A sites). This interaction is dependent upon the electronic configuration of the cations concerned. This result shows that the near crystal field environment (octahedral or tetrahedral) of the ferric ions alone does not control the activity and that the divalent ions also have a definite role in governing the resultant catalytic activity. Detailed discussion of the influence of magnetic ordering and exchange interactions on catalytic activity for the oxidation of CO has been given elsewhere<sup>10</sup>.

The linear relationship between unit cell dimensions of ferrites and the logarithm of the rate constant at 280°C is in favour of the redox mechanism because the metal-oxygen bond length increase is equivalent to the decrease in bond energy. This aspect is clear in the correlation obtained between activity

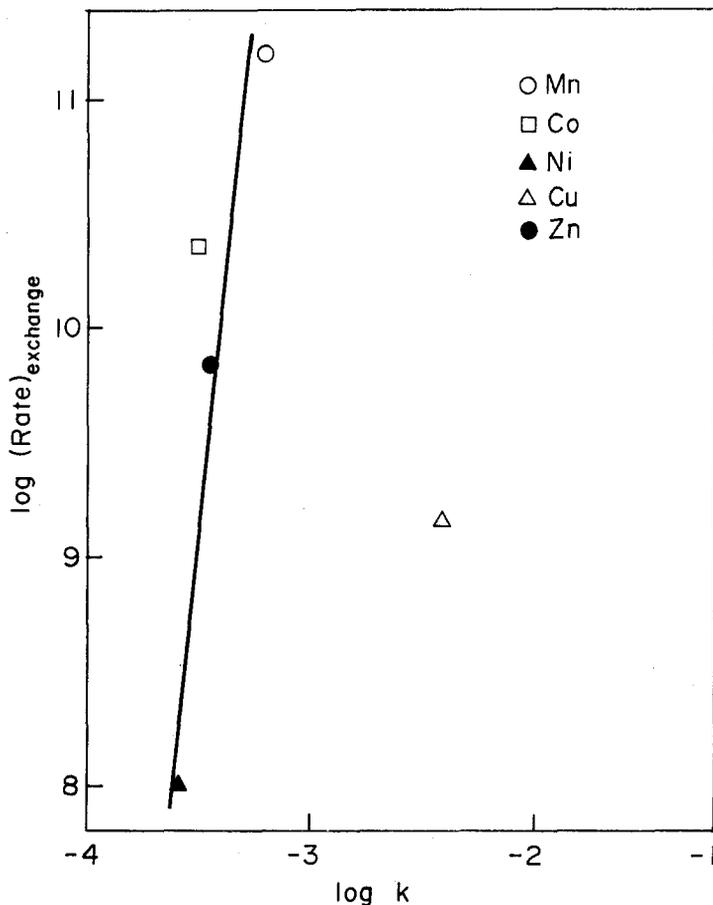
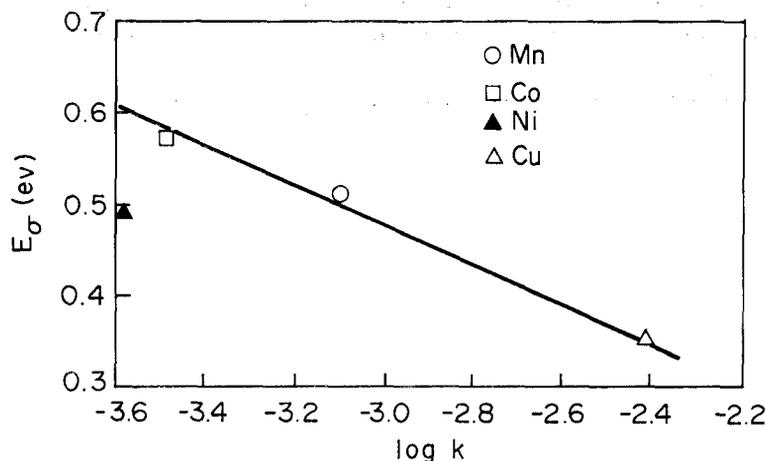


Fig. 4. Relationship between surface oxygen bond energy and activity of simple ferrites.

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**Fig. 5.** Correlation between activation energy for electrical conductivity and activity.

and surface oxygen bond energy (characterised by the values of the rate constants for homonuclear isotopic oxygen exchange at 300°C as reported by BORESKOV<sup>(11)</sup>) shown in Fig. 4. The inverse relationship between the activity and the activation energy ( $E_a$ ) for electrical conductivity also supports that the charge transfer step controls the overall kinetics of the reaction.

In conclusion it may be stated that the ferric ions at both tetrahedral and octahedral sites function as active centres for the oxidation of CO and the divalent ions at these two sites participate in determining the resultant activity through crystal field effects.

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