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MECHANISM OF OXIDATION OF CARBON MONOXIDE ON SPINEL TYPE FERRITES

By

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Abstract

Kinetic studies on the oxidation of CO by ferrites show that the reaction is first order with respect to CO partial pressure and zero order with respect to O₂ and CO₂ partial pressures. IR, electrical conductivity and adsorption studies show that CO gets adsorbed on the catalyst surface as CO⁺, which reacts with oxygen to give rise to various types of carbonate species. These decompose at high temperatures to form CO₂. The elementary steps involved in the reaction are postulated, and it has been shown that the step involving the adsorption of CO as a positive species is rate determining.

Introduction

Spinel type ferrites of the general formula MFe₂O₄ are an emerging class of catalysts with application in processes like hydrodesulphurization (1), dehydrogenation of butene to butadiene (2) and the treatment of automobile exhaust gases (3). The points of fundamental interest about ferrite-catalysts relate mainly

1. to the precise seat of catalytic activity
2. to the role played by the divalent metal ion M²⁺ and
3. to the cation distribution or degree of inversion.

Divergent views have emerged from some recent studies (4-6) on these aspects. Hence, a systematic investigation of the catalytic oxidation of carbon monoxide on simple ferrites of the type MFe₂O₄ (M=Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) and on mixed ferrites of the type Ni_xZn_{1-x}Fe₂O₄ (x=0.2, 0.5, 0.8) has been undertaken not only to examine the solid state aspects stated above, but also to establish the relative roles of adsorbed oxygen and lattice oxygen in the oxidation step, because of the technical importance

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of this reaction in the treatment of automobile exhaust gases and of its interesting mechanistic aspect, *e.g.*, the simultaneous participation of oxygen from the gas phase, adsorbed state or lattice oxygen, depending on the catalyst and experimental conditions used.

Experimental

The ferrite catalysts, except MnFe_2O_4 and Fe_3O_4 , were prepared by the coprecipitation technique described by Boroskov *et al* (8). MnFe_2O_4 was prepared by solid state reaction between MnCO_3 and Fe_2O_3 , Fe_3O_4 using the method adopted by David and Welch (9).

Measurements of electrical conductivity and Seebeck coefficient in air and other ambient atmospheres were carried out using specially designed cells. Magnetic susceptibility measurements were done using a Faraday balance and the cation distribution was computed from the intensities of the X-ray diffraction lines by the method of Bertaut (10).

CO was prepared by the reaction of CaCO_3 and Zn dust at around 700°C . O_2 , He, and CO_2 were obtained from commercial sources. All gases were purified by standard procedures before use.

An all-glass reactor with gas recirculation device, was used for kinetic measurements. For IR studies, self-supporting discs of the catalyst were prepared by pressing ~ 80 mg of the sample at about 8 tons/cm^2 . The discs were exposed to various gases under different experimental conditions and the spectra recorded in the range $800\sim 2400 \text{ cm}^{-1}$ using a Beckman IR-12 double beam spectrometer. The adsorption studies were carried out by the conventional volumetric method.

Results

Kinetic studies:

From detailed studies on the Kinetics of the oxidation of CO, with different mixtures of CO and O_2 in the temperature range $200\sim 480^\circ\text{C}$, and at various initial total pressures ($4\sim 14 \text{ cm Hg}$), it has been established that the reaction is first order with respect to CO partial pressure and zero order with respect to O_2 partial pressure. Details of the kinetic results have been reported earlier (11). Also added CO_2 does not affect the rate of the reaction. The first order rate equation

$\text{Rate} = K P_{\text{CO}}$ is applicable to simple as well as mixed ferrites.

Electrical conductivity:

In oxygen atmosphere, *p*-type ferrites like NiFe_2O_4 and CoFe_2O_4 show

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an increase in the value of electrical conductivity while *n*-type ferrites namely ZnFe_2O_4 , MnFe_2O_4 and CuFe_2O_4 show a decrease. (Fig. 1) This indicates that oxygen is adsorbed on the catalyst as acceptor species, *i.e.*, as O^- or O_2^- . Then changes in electrical conductivity for the adsorption on ferrites are small, indicating a relatively low uptake of oxygen.

All ferrites give rise to the formation of CO_2 when CO alone is admitted to the system above 200°C , showing that the ferrite surface is getting reduced to a considerable extent.

For *n*-type ferrites, the conductivity increases with CO pressure indicating the formation of a positively charged species (CO^+) as a consequence of electron transfer from CO to the catalyst.

In the case of *p*-type ferrites there is a decrease in conductivity upto 2 cm Hg pressure, *i.e.*, CO is adsorbed as CO^+ . Then there is an increase in conductivity which is probably due to the formation of an 'inversion layer', as a result of excess cation concentration at the surface (surface reduction). The conductivity changes observed are shown in Fig. 2.

On all ferrites the adsorption of CO_2 (Fig. 3) results in very slight decrease of conductivity denoting that the adsorption of CO_2 is very small.

During the reaction between CO and O_2 , the *n*-type ferrites register an increase in conductivity with respect to time while *p*-type ferrites show a decrease, the trends being similar to those accompanying the adsorption of CO. The variations of conductivity change as a function of time under reaction conditions are shown in Fig. 4. However, in the case of *n*-type ferrites the observed increase is several times less than that observed during CO adsorption. Hence it may be concluded that the ferrite do not undergo any significant reduction during reaction but function essentially in the oxidised state. The transient reduced state that might be formed during the reaction is quickly restored to the oxidised state either by the oxygen available in the gas phase or by that in the adsorbed state.

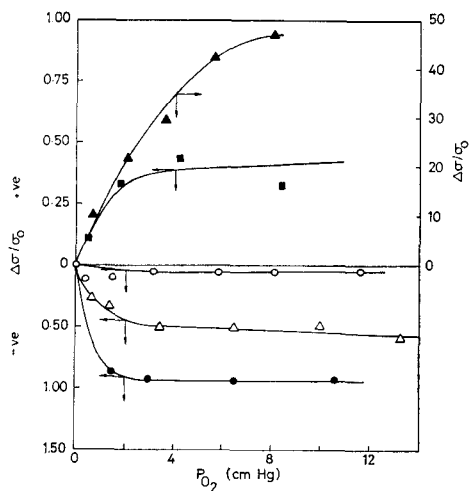


Fig. 1. Changes in the electrical conductivity of ferrites in oxygen atmosphere.

- MnFe_2O_4 (440°C) ■ CoFe_2O_4 (280°C)
- ▲ NiFe_2O_4 (260°C) △ CuFe_2O_4 (260°C)
- ZnFe_2O_4 (300°C)

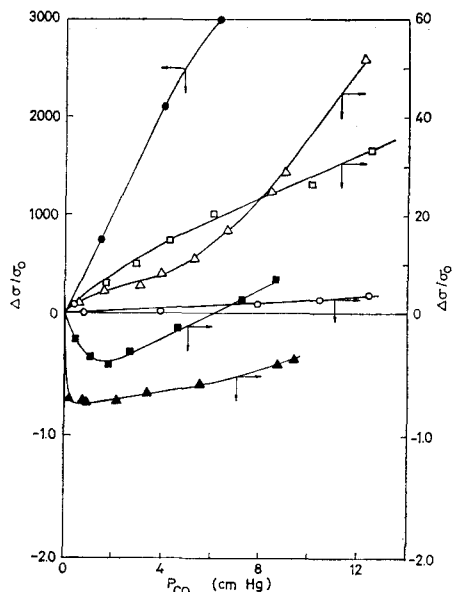


Fig. 2. Variation of electrical conductivity changes of ferrites in CO atmosphere.

- | | |
|-------------------------------------|-------------------------------------|
| ○ MnFe_2O_4 (440°C) | □ Fe_3O_4 (160°C) |
| ■ CoFe_2O_4 (280°C) | ▲ NiFe_2O_4 (260°C) |
| △ CuFe_2O_4 (260°C) | ● ZnFe_2O_4 (300°C) |

Adsorption studies

Adsorption of oxygen on all ferrites except NiFe_2O_4 is very small and independent of the equilibrium pressure, showing that the adsorption is fast and reaches saturation at low values of uptake. This is in accordance with the zero order dependence of the rate of CO oxidation on oxygen partial pressure.

The values of activation energy for the adsorption of CO on CoFe_2O_4 and ZnFe_2O_4 are 10.5 and 15.5 kcal/mole respectively which are comparable to the values obtained for the oxidation of CO on these ferrites namely, 7 and 12 kcal/mole. Kinetics of CO adsorption were studied for 100 minutes. Then the CO was pumped out, oxygen admitted and the kinetics of adsorp-

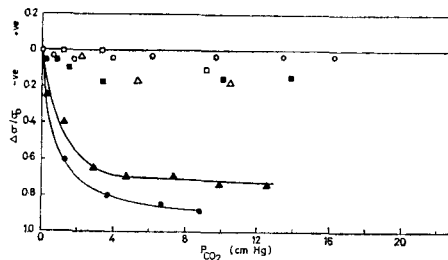


Fig. 3. Changes in the electrical conductivity of ferrites in CO_2 atmosphere.

- | | |
|-------------------------------------|-------------------------------------|
| ○ MnFe_2O_4 (440°C) | ▲ Fe_3O_4 (160°C) |
| □ CoFe_2O_4 (280°C) | ■ NiFe_2O_4 (260°C) |
| △ CuFe_2O_4 (260°C) | ● ZnFe_2O_4 (300°C) |

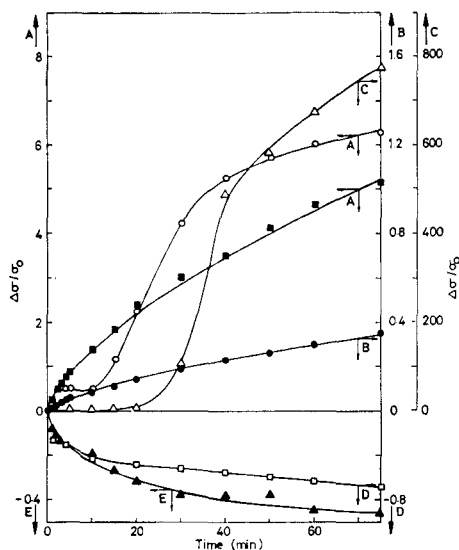


Fig. 4. Changes in the electrical conductivity of ferrites during CO oxidation.

- | | |
|-------------------------------------|-------------------------------------|
| ● MnFe_2O_4 (440°C) | ■ Fe_3O_4 (160°C) |
| □ CoFe_2O_4 (280°C) | ▲ NiFe_2O_4 (260°C) |
| ○ CuFe_2O_4 (260°C) | △ ZnFe_2O_4 (300°C) |

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TABLE 1 Rates of uptake of CO and O₂ on Ferrites

Rates for (min ⁻¹)	CoFe ₂ O ₄ (280°C)	NiFe ₂ O ₄ (260°C)	ZnFe ₂ O ₄ (300°C)
Uptake of CO	8×10 ⁻³	8×10 ⁻³	3×10 ⁻²
Subsequent uptake of O ₂ on CO presorbed surface	47×10 ⁻³	33×10 ⁻³	17×10 ⁻²

TABLE 2 IR Studies

Pre-treatment condition	Temperature (°C)	IR adsorption, observed bands in cm ⁻²	The bands are assigned to	Remarks
Adsorption of oxygen	230-280	Nil	—	Background absorption in the case of ZnFe ₂ O ₄ in the range 900-1200 cm ⁻¹
Adsorption of CO after oxygen pre-treatment at higher temperature	30	860, 1320, 1340, 1265, 1380, 1460, 1475, 1525, 1540	Monodentate species	Band around 1060 cm ⁻¹ is masked by background absorption
		830, 1280, 1560, 1580, 1640, 1655	Bidentate species	Bands around 1030 and 1150 cm ⁻¹ masked by background absorption
		1420 and 1435	Uncoordinated CO ₃ ²⁻	
		2079	Carbonyl species	Observed only with NiFe ₂ O ₄
		2175	M-CO ⁺	
Catalyst exposed to CO for 30 minutes	230-280	2360	Weakly adsorbed CO ₂	Bands at 1320, 1340, 1420, 1440, 525 are absent. Intensities of other bands due to carbonate species are also decreased.
CO and O ₂ mixture	30	All bands due to carbonate	—	No bands due the adsorbed CO ₂
CO and O ₂ mixture	230-280	2360 All bands due to carbonate species	Weakly adsorbed CO ₂	Bands at 2170 cm ⁻¹ M-CO ⁺ and 2070 (carbonyl species) are absent. The band at 2170 cm ⁻¹ appears at 180°C. The intensities of the bands due to carbonate species is constant with time.
Pure CO ₂ and O ₂ mixture	280	2360	Gaseous or weakly held CO ₂	

tion of oxygen studied. These studies show that the rate of adsorption of O_2 on a surface containing presorbed CO is higher than the rate of adsorption of CO, *i.e.*, the reoxidation of the surface as well as the surface reaction between adsorbed CO and oxygen (adsorbed or gas phase) are faster than the adsorption of CO (Table 1). This supports the fact that the reaction is first order with respect to CO partial pressure.

IR Studies:

The bands obtained on admitting CO to the catalyst (previously conditioned at $230\sim 280^\circ C$ with 1 Torr of oxygen) at room temperature can be attributed to several carbonate species and the $M-CO^+$ species (Table 2). At higher temperatures some of the bands attributed to the carbonate species and to the $M-CO^+$ species disappear and bands due to adsorbed CO_2 appear. Typical spectra obtained under these experimental conditions are given in Fig. 5.

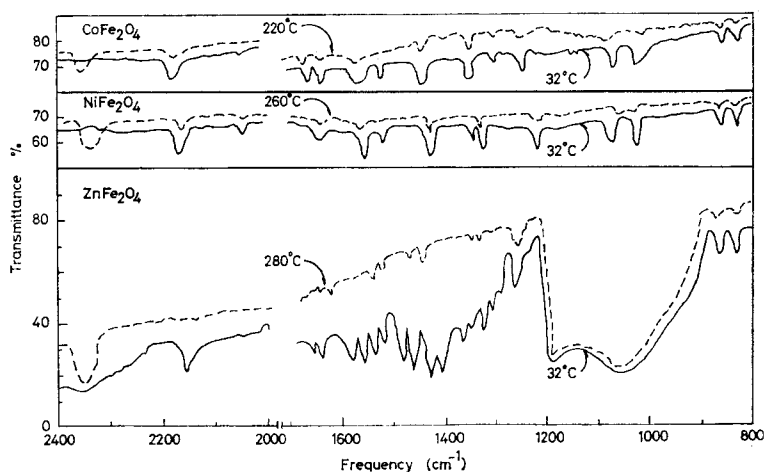


Fig. 5. Infrared spectra of ferrites after adsorption of CO.

When the reaction mixture ($CO + O_2$) is introduced under reaction conditions, bands similar to those obtained on CO adsorption are obtained but there is no band attributable to $M-CO^+$. Also a band characteristic of weakly adsorbed CO_2 (2360 cm^{-1}) is observed.

IR studies on the catalyst exposed to a mixture of CO_2 and O_2 show bands due to adsorbed CO_2 but none attributable to the carbonate species.

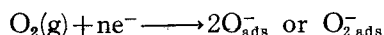
These results show that CO gets adsorbed on the catalyst surface as CO^+ . The adsorbed CO reacts with oxygen to give various types of carbonate species, which decompose at high temperatures to produce CO_2 .

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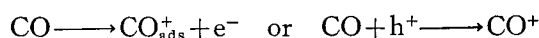
Mechanism of oxidation:

On the basis of the above observations, the elementary steps involved in the CO oxidation on ferrite catalysts may be written as follows:

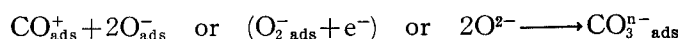
1. Chemisorption of oxygen



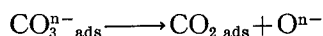
2. Chemisorption of CO



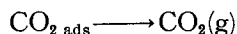
3. Formation of carbonate species



4. Decomposition of carbonate species to yield CO_2 (ads)



5. Desorption of CO_2



Except for step (2), other steps cannot be rate controlling because of the following reasons:

1. The extent of oxygen adsorption on ferrites is low and the reaction is zero order with respect to oxygen partial pressure.
Reoxidation of the surface after CO adsorption as well as surface reaction between the adsorbed CO and oxygen are faster than the adsorption of CO, *i. e.*, step (3) is faster than step (2). This is confirmed by the IR data as follows: Carbonate species are formed both at low and high temperatures even in the absence of gas phase oxygen (Table 2). The IR band at 2175 cm^{-1} , characteristic of CO^+ species is observed during the adsorption of CO at room temperature but it is absent at higher temperatures. This indicated that at reaction temperature the CO^+ species reacts quickly to form the carbonate species.
2. The concentration of the carbonate species under reaction conditions is very small (IR studies), and so, they decompose fast to give CO_2 .
3. The reaction is not inhibited by the product CO_2 .

The step involving the adsorption of CO as a positive species, is the rate determining step. This conclusion is supported by the following observations.

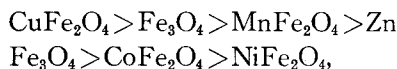
1. The reaction is 1st order with respect to CO partial pressure.
2. The activation energies of CO adsorption and CO oxidation are comparable.

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- Electrical conductivity change during reaction and CO adsorption are in the same direction.

As the metal-oxygen bond length increases, the M-O bond energy decreases. This facilitates charge transfer from CO to the metal ion, which is the rate determining step. Hence, the activity for CO oxidation increases with increase of bond distance. The rate constant for homonuclear exchange has been used to characterise the oxygen bond energy. The linear relationship obtained between homonuclear exchange and activity (Fig. 6) brings out clearly the role of surface oxygen bond energy in governing the rate of oxidation.

The observed activity pattern is



showing the inverse spinels (CuFe_2O_4 and Fe_3O_4) to be more active than the nearly normal spinel MnFe_2O_4 and the normal ferrite ZnFe_2O_4 .

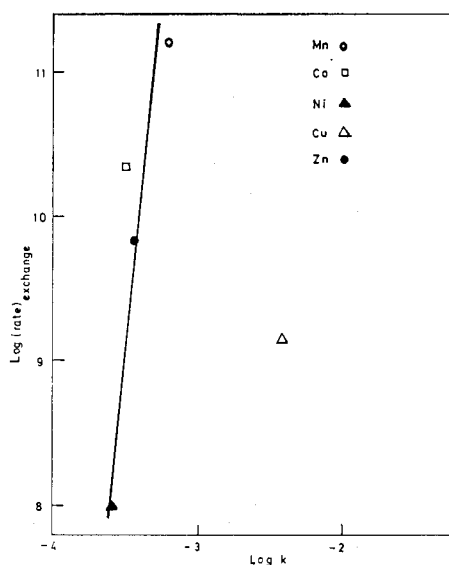


Fig. 6. Correlation between rate of homonuclear isotopic oxygen exchange and activity of ferrites.

Acknowledgement

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