

Catalytic Oxidation of CO Gas over Nanocrystallite $\text{Cu}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$

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Abstract The catalytic oxidation of CO over nanocrystallite $\text{Cu}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ powders was studied using advanced quadruple mass gas analyzer system. The oxidation of CO to CO_2 was investigated as a function of reactants ratio and firing temperature of ferrite powders. The maximum CO conversion was observed for ferrite powders which have equal amount of Cu^{2+} and Mn^{2+} ($\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$). The high catalytic activity of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ can be attributed to the changes of the valence state of catalytically active components of the ferrite powders. The firing temperature plays insignificant role in the catalytic activity of CO over nanocrystallite copper manganese ferrites. The mechanism of catalytic oxidation reactions was studied. It was found that the CO catalytic oxidation reactions on the surface of the $\text{Cu}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ was done by the reduction of the ferrite by CO to the oxygen deficient lower oxide then re-oxidation of this phase to the saturated oxygen metal ferrite again.

Keywords CO · Catalytic oxidation · Ferrites ·
 $\text{Cu}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ · Nanocrystallite

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1 Introduction

Nowadays CO, volatile organic compounds and polyaromatics are ubiquitous air pollutants that give rise to deleterious health and environmental effects. However, emission of carbon monoxide gas in industrial processes, motors engines and even by a burning cigarette is one of the most significant environmental problems. Catalytic oxidation processes are considered to be an effective approach in controlling these emissions where CO is converted to CO_2 which is much less harmful than carbon monoxide. This conversion includes different chemical and physical processes which take place simultaneously and have a profound influence on each other. The conversion can be carried out in presence of oxygen and catalyst at low temperatures. The catalyst used in the oxidation process should be non volatile, cheap in price, highly active and stable in prevailing conditions. These requirements are achieved by nanosized ferrite materials which show good response towards oxidation of CO to CO_2 .

Since most of researches on ferrites highlight on the development of advanced ferrite materials which satisfy specific requirements in different industrial applications, many attempts have been done to synthesize and investigate pure and substituted copper ferrite [1–7]. It was found that such kinds of ferrites are characterized by a spinel structure with high thermodynamic stability, electrical conductivity and high catalytic activity.

Shaheen et al. [8] measured the catalytic activity of the obtained pure and mixed oxides of $\text{CuO-Fe}_2\text{O}_3$ for the decomposition of H_2O_2 at 30–50 °C. It was found that the mixed oxide solids have catalytic activity higher than single oxides preheated at 350 and 550 °C. The rise in precalcination temperature to 750 and 1,000 °C brought about a drastic decrease in the activity of mixed solids

because of the formation of copper ferrite phase and/or sintering process.

The ferros spinels of nickel, cobalt, copper and their sulphated analogues [9] were prepared by the room temperature coprecipitation route to yield samples with high surface areas. Onuchukwu [10] showed that Metal-doped copper ferrite spinel oxide series, $M_xCu_{1.5}Fe_{1.5}O_4$, are precursors adopted recently to enhance the efficiency of catalysts in energy industries. The non-stoichiometric spinel copper ferrite $Cu_xFe_{3-x}O_4$ series ($x \leq 3$) were earlier accredited superior to all simple mono-metal oxides including Ag_xO .

Although the kinetics and mechanism of catalytic oxidation of CO to CO_2 were investigated by many researchers using different kinds of catalysts [11–16], many of related phenomena are not yet fully understood.

The purpose of this work is to study the effect of ferrite components and firing temperature of ferrite powders on the catalytic activity of copper manganese ferrite ($Cu_xMn_{(1-x)}Fe_2O_4$) towards the oxidation of carbon monoxide to carbon dioxide.

2 Experimental

The nanocrystallite $Cu_xMn_{(1-x)}Fe_2O_4$ samples were prepared by dry technique using highly purified CuO , MnO_2 and Fe_2O_3 . Pre-calculated amounts of (–250) mesh CuO , MnO_2 and Fe_2O_3 were mixed with an amount of substituting $Cu_xMn_{1-x}Fe_2O_4$ ($X = 0.0, 0.5$ and 1.0) to prepare $MnFe_2O_4$, $CuFe_2O_4$ and $Cu_{0.5}Mn_{0.5}Fe_2O_4$. The blend was thoroughly mixed in a ball mill for 1 h with 50 wt% ethanol in order to get an intimate blending and homogenization. The mixture was then crushed and dried at 80 °C for 1 h and the produced powder was left overnight. The samples were fired in a muffle furnace fitted with an on/off temperature controller. The temperature sensor was 13% pt/pt-Rh thermocouples. The maximum deviation of the thermocouple reading from the set point was 20 °C at 1,300 °C. Samples were placed in high alumina refractory holders then introduced in the hottest zone of the furnace. After proper soaking for periods of 4 h at 1,000, 1,100 and 1,200 °C, the powder was left to cool gradually to room temperature to avoid cracking due to thermal shocks. The different phases formed at different temperatures were identified by XRD technique using a JSX-60P JEOL diffractometer with a copper target. Samples were subjected to ball milling for 3 h and the average crystallite size was calculated using the diffractions peaks from Scherer's formula [17] as shown below;

$$D = 0.9 \lambda / (\beta - \beta_1) \cos \theta$$

where D is the grain diameter, β is the half-intensity width of the relevant diffraction peak, β_1 represents the half-intensity width due to instrumental broadening, λ is the X-ray wave length, and θ is the angle of diffraction. The crystal size of ferrite samples also were investigated by TEM images using JEOL (JSM5410).

The experimental apparatus of CO catalytic oxidation used pure CO gas obtained by passing CO_2 over coke in a tube furnace at 1,100 °C. The produced CO is purified by soda lime to absorb any traces of CO_2 and silica gel to remove moisture. 300 mg of the sample was held between two pieces of quartz wool in a tubular horizontal flow reactor (i.d.10 mm). The reactor was heated in tube furnace up to constant temperature (400 °C). The reactor was held at that temperature for about 30 min. before the onset of the experiment to refresh the catalyst. A mixture of CO, O_2 and N_2 gas was passed over the catalyst at a constant rate of 0.5 L/min. The outlet gas was analyzed using advanced on-line quadruple mass spectrometer (Hiden-Analytical, Warrington, UK) which continuously monitors the gases with time.

3 Results and Discussion

3.1 XRD Analysis

The results of XRD analyses of the prepared ferrite powders fired at temperatures 1,000–1,200 °C are shown in Table 1. At all temperatures, Mn-ferrite is the only phase detected at $x = 0.0$ whereas at $x = 1$, the most predominant phase is $CuFe_2O_4$.

The average crystallite size of ferrite powders were calculated from X-ray diffraction data. The ferrite powders show very low crystal size, 50 nm. The crystal size of ferrite samples were also investigated by TEM images as shown in Fig. 1 for nanocrystallite $Cu_{0.5}Mn_{0.5}Fe_2O_4$

Table 1 XRD parameters for $Cu_xMn_{1-x}Fe_2O_4$

Sample	X	d	I	2θ	
T = 1,000 °C	$CuFe_2O_4$	1.0	2.51	100	35.7
	$Mn_{0.5}Cu_{0.5}Fe_2O_4$	0.5	2.50	100	35.8
	$MnFe_2O_4$	0.0	2.69	100	33.2
T = 1,100 °C	$CuFe_2O_4$	1.0	2.51	100	35.7
	$Mn_{0.5}Cu_{0.5}Fe_2O_4$	0.5	2.51	100	35.8
	$MnFe_2O_4$	0.0	2.70	100	33.1
T = 1,200 °C	$CuFe_2O_4$	1.0	2.52	100	35.6
	$Mn_{0.5}Cu_{0.5}Fe_2O_4$	0.5	2.52	100	35.6
	$MnFe_2O_4$	0.0	2.69	100	33.2

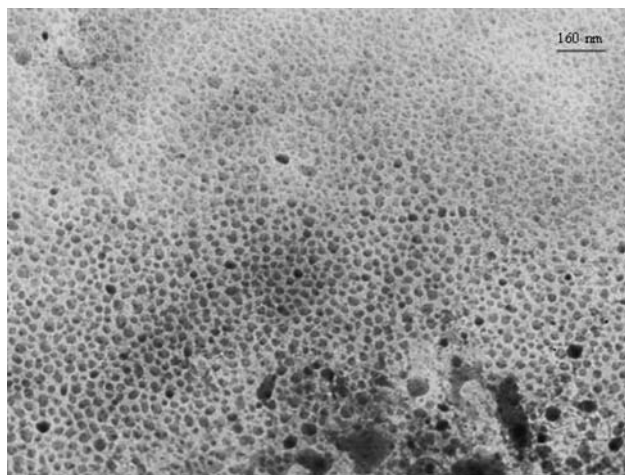


Fig. 1 TEM image of nanocrystallite $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ sample fired at $1200\text{ }^\circ\text{C}$

powder fired at $1,200\text{ }^\circ\text{C}$, which clarify the presence of homogenous sizes with average crystallite size $\sim 50\text{ nm}$.

3.2 Effect of Structure Changes on the Catalytic Oxidation Process

The catalytic activity of nanocrystallite $\text{Cu}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ ($X = 0, 0.5$ and 1) was investigated through the oxidation of CO to CO_2 as a function of reactant ratio and firing temperature. The degree of conversion of CO to CO_2 is estimated from the following equation;

$$\text{CO conversion extent (\%)} = \frac{\text{CO}_i - \text{CO}_t}{\text{CO}_i} \times 100$$

where CO_i is the initial CO concentration, CO_t is the CO concentration at time t . The efficiency of using $\text{Cu}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ as a catalyst for oxidation process of CO can be defined by the maximum degree of conversion of CO to CO_2 .

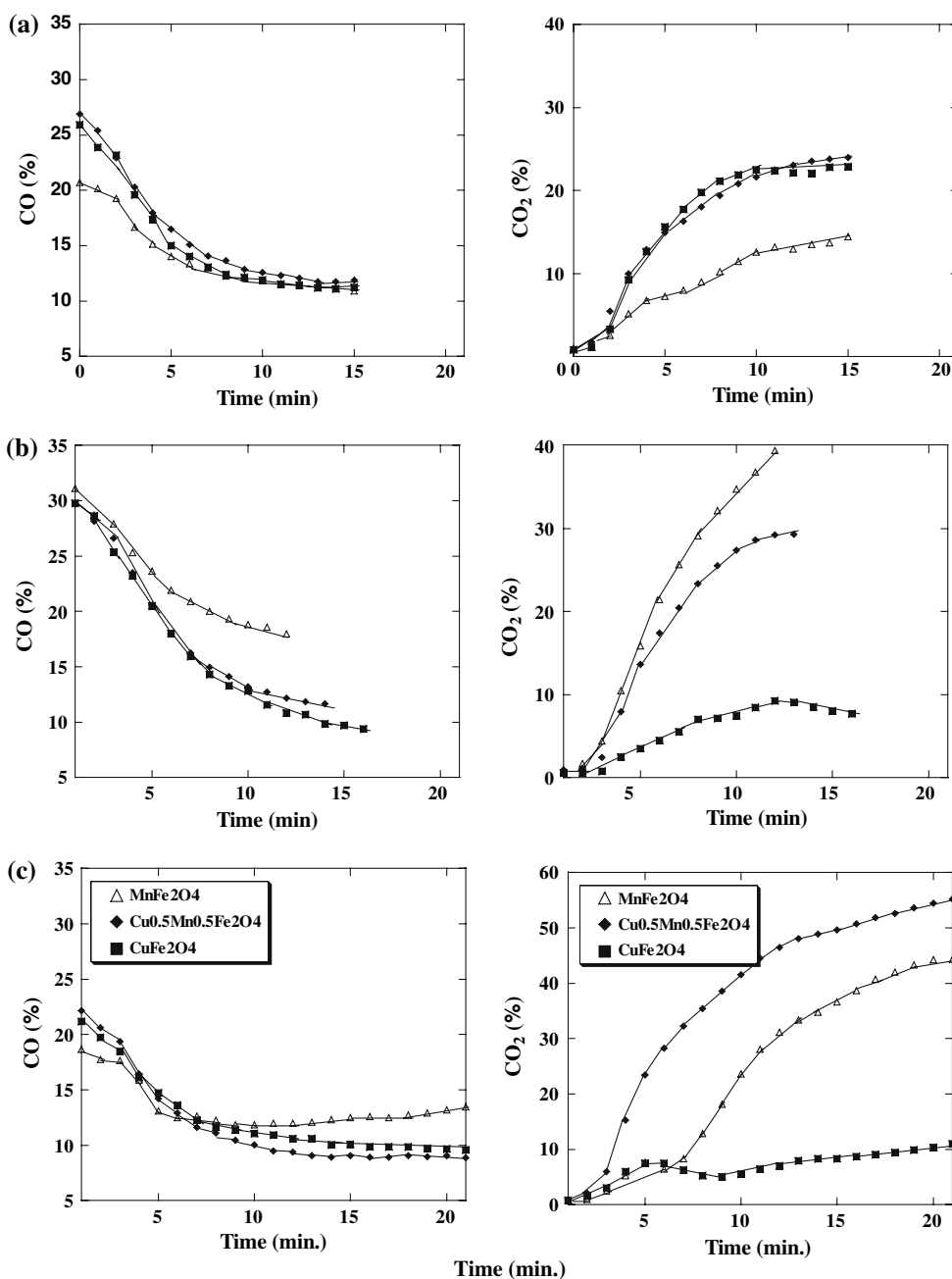
The crystallite size of ferrite samples plays a significant role in the catalytic oxidation of CO. The prepared powders with large crystal size (200 nm) were tested for catalytic oxidation of CO and showed a very low catalytic activity ($\sim 15\%$). Accordingly, the samples were subjected to ball milling for 3 h to get ferrite powders in nanosize range (50 nm).

The influence of ferrite components on the catalytic oxidation of CO was studied using three kinds of ferrite powders namely CuFe_2O_4 , MnFe_2O_4 and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$. The typical variations of gas composition (CO and CO_2) as a function of time are shown in Fig. 2 for ferrite powders fired at $1,000$ – $1,200\text{ }^\circ\text{C}$. Generally, it can be observed that for all ferrite powders, as the time increases, the CO gas concentration decreases from about 20%

or 30% to about 10% within 15–20 min. In accordance, the CO_2 concentration increases from about 0.0 to reach 10–50% in the gas mixture. The variation of catalytic activity of ferrite powders with different Cu^{2+} concentration as a function of time is observed in Fig. 3. It can be reported that the percentage of CO conversion increases by time till a maximum value and then become constant owing to poisoning of catalyst. MnFe_2O_4 samples show low response towards CO oxidation (30–40% efficiency within 10 min), while the response towards catalytic oxidation is increased with increasing Cu^{2+} content in the ferrite powders to certain extent. To clarify the effect of Cu^{2+} concentration on the efficiency of catalytic oxidation of CO, $\text{Cu}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ powders fired at $1,000\text{ }^\circ\text{C}$ with different Cu^{2+} contents ($x = 0.0, 0.3, 0.5, 0.7$ and 1.0) were tested and the efficiency of the catalytic oxidation process was estimated from the maximum value of CO conversion (%) as shown in Fig. 4. The maximum CO conversion (efficiency, %) was observed for ferrite samples which have equal amount of Cu^{2+} and Mn^{2+} ($\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$). The efficiency of catalytic activity of ferrite powders at different Cu^{2+} concentration reflects the effect of structure changes of ferrite on the catalytic oxidation of CO to CO_2 . The Mn-ferrite powders ($x = 0.0$) as well as Cu–Mn ferrites with $x = 0.3$ and $x = 0.7$ show a low efficiency less than 50%. It can be reported that the efficiency increased with increasing Cu content till reach maximum efficiency of catalytic activity for $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ samples. Further increases in Cu^{2+} content will decrease the catalytic activity (35% for $\text{Cu}_{0.7}\text{Mn}_{0.3}\text{Fe}_2\text{O}_4$). The Cu-ferrite powders show a good response toward catalytic oxidation of CO and result 59% efficiency.

The variation of catalytic oxidation reactions of CO with structure changes can be explained in terms of the concept of bivalent catalytic centers theory [8]. It was found that the catalytic activity of the mixed Cu–Fe–Mn mixtures obtained by thermal treatment of the $\text{CuO-MnO}_2\text{-Fe}_2\text{O}_3$ at the same calcinations temperatures is greater than that of single crystal. The centers of CuO consist of $\text{Cu}^{2+}\text{-Cu}^+$ ion pairs while the centers of MnO_2 contain $\text{Mn}^{4+}\text{-Mn}^{2+}$ ion pairs and that of Fe_2O_3 consist of $\text{Fe}^{3+}\text{-Fe}^{2+}$ ion pairs. The higher catalytic activity of the three component oxides can be attributed to the fact that beside the one component sites $\text{Cu}^{2+}\text{-Cu}^+$, $\text{Mn}^{4+}\text{-Mn}^{2+}$ and $\text{Fe}^{3+}\text{-Fe}^{2+}$ there will be also the mixed sites $\text{Mn}^{4+}\text{-Cu}^{1+}\text{-Fe}^{2+}$ and/or $\text{Cu}^{2+}\text{-Fe}^{3+}\text{-Mn}^{2+}$ ion pairs as a result of mutual charge interaction [8]. In other words, increasing activity of the mixed oxides might be attributed to the increase in the concentration of active sites via creation of new ion pairs. This means that the variation of catalytic activity of ferrite powders ($\text{MnFe}_2\text{O}_4 < \text{CuFe}_2\text{O}_4 < \text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$) are probably due to the changes of the valence state of catalytically active components of the ferrite powders.

Fig. 2 Variation of gas composition (CO and CO₂) with time for ferrite powders fired at; (a) 1,000 °C (b) 1,100 °C (c) 1,200 °C

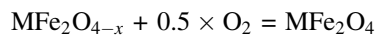
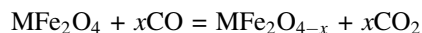


3.3 Effect of Firing Temperature

The influence of firing temperature on the catalytic oxidation of CO over nanocrystallite Cu–Mn ferrite powders is shown in Fig. 5. The results show that firing temperatures slightly affect the catalytic oxidation of CO. However, it can be noticed that the catalytic oxidation of CO using Cu–Mn ferrite increases with increasing calcinations temperature from 1,000 °C to 1200 °C due to high crystallization and complete formation of the ferrite phase.

3.4 Mechanism of Catalytic Oxidation of CO

The catalytic oxidation reactions of carbon monoxide by metal ferrite can be written in the following equations;



where M is the metal.

According to the contact catalysis theory [18] the surface reaction involves five consecutive steps (i) Diffusion of CO and O₂ to the surface of the ferrite, (ii) The gas

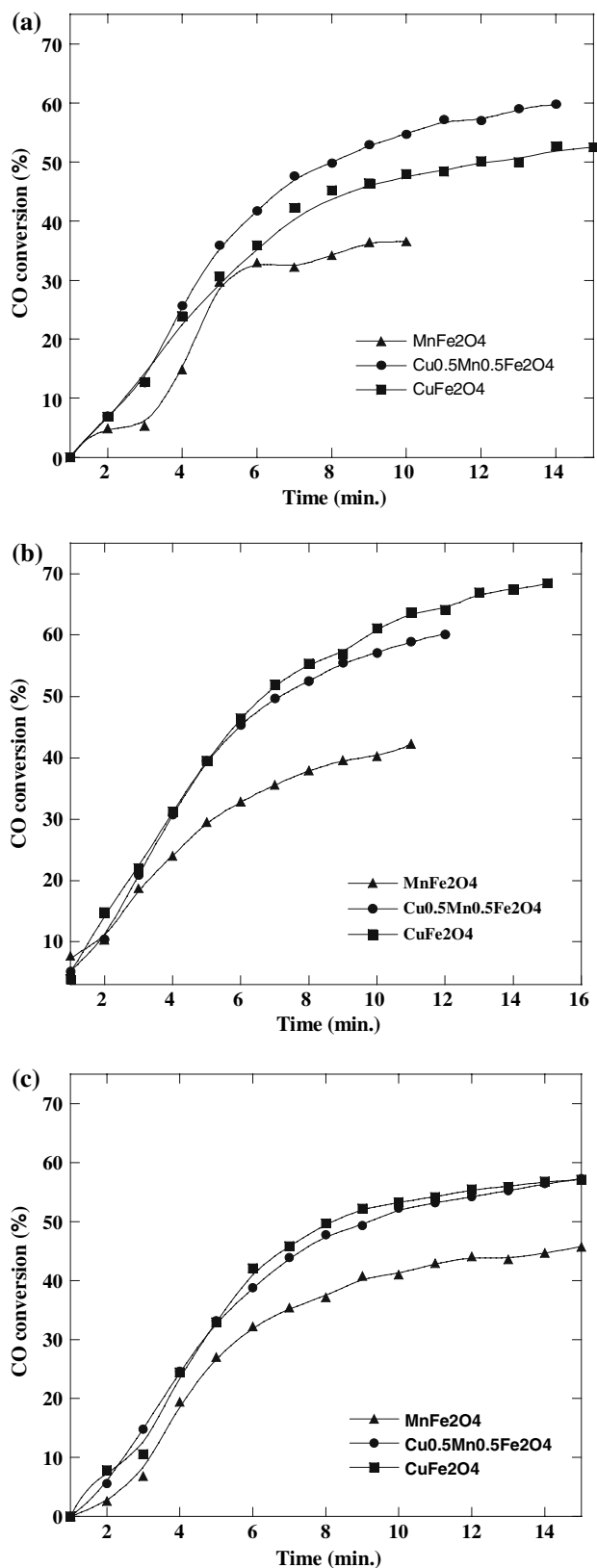


Fig. 3 Variation of CO conversion with time for ferrite powders; (a) fired at 1,000 °C (b) fired at 1,100 °C (c) fired at 1,200 °C

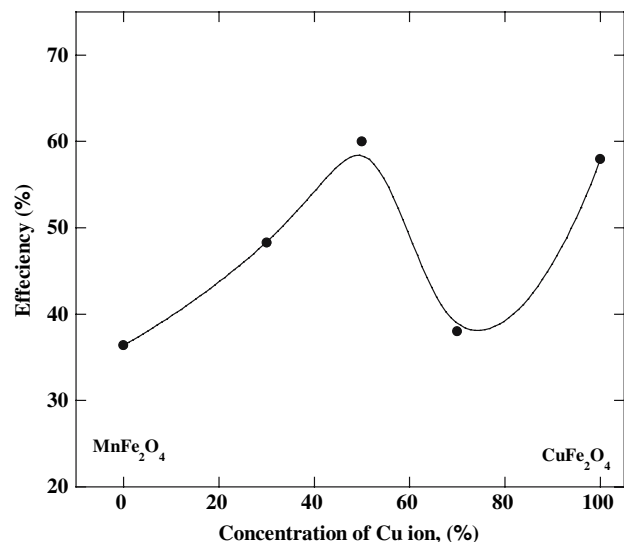


Fig. 4 Effect of Cu²⁺ concentration on the efficiency of catalytic activity of ferrite powders fired at 1,000 °C

molecules adsorb preferentially on the surface of the ferrite and due to chemisorption of gas molecules, the oxygen in the ferrite transfer from the bulk to the chemisorbed species, (iii) CO₂ is produced by the reaction of CO and O₂ on the surface of the catalyst, (iv) The produced CO₂ molecules are then released from the interface and leave sites for other CO and O₂ gas molecules adsorption, (v) Finally the produced gas diffused into the main body of the gas.

In other words, carbon monoxide, on coming in contact with a readily reducible oxide, is almost instantly adsorbed by primary valence forces, forming a surface complex which can decompose either into the original substances or into the reduction products, depending on the conditions. At higher temperatures the rate of decomposition of the surface complex into the reaction products is extremely rapid but at comparatively low temperatures it becomes so slow that at any instant a large fraction of the surface is covered with this adsorbed layer of carbon monoxide molecules. At still lower temperatures carbon monoxide is adsorbed less and less by primary valence and more and more by secondary. The latter, however, is not a preliminary stage in the reduction, except in so far as a primary valence union results from the secondary type by a shift of electrons.

To confirm this conclusion, reduction experiments were done isothermally by pure carbon monoxide gas for different ferrite samples at 400 °C using a thermogravimetric technique. The reduction behavior of samples was followed up by measuring the oxygen weight-loss as a function of time as shown in Fig. 6. The reduction experiments indicate that carbon monoxide reduces the samples at the same temperature of the catalytic process and the rate of

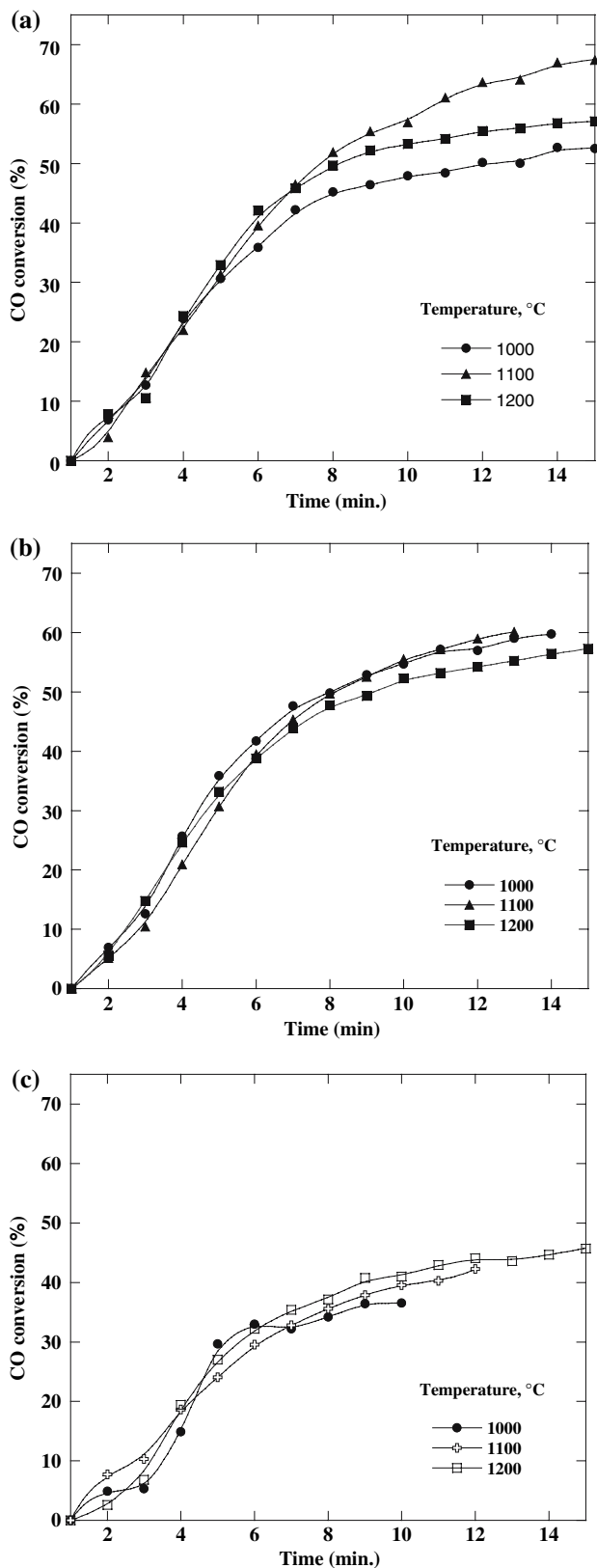


Fig. 5 Variation of CO conversion with time for ferrite powders fired at 1,000–1,200 °C; (a) CuFe₂O₄ (b) Cu_{0.5}Mn_{0.5}Fe₂O₄ (c) MnFe₂O₄

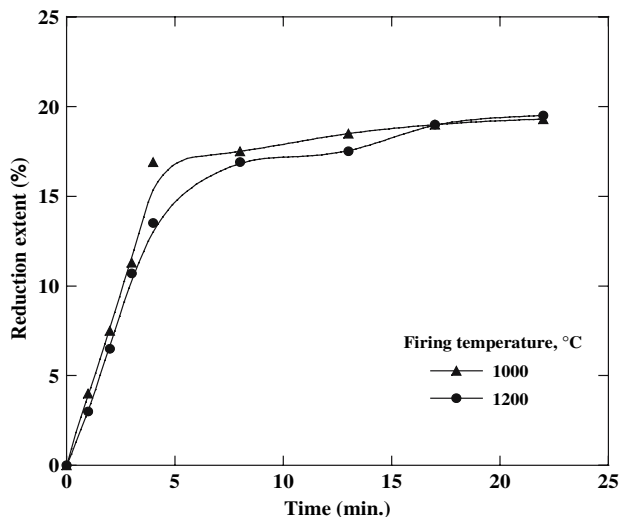


Fig. 6 Isothermal reduction behavior of Cu–Mn ferrite powders in CO gas at 400 °C

reduction behaves similarly with the catalytic process as it starts quickly and slows down as time proceeds.

For metal oxide pellets many reaction rate models were reported [19–24]. The grain model equations developed by Szekely [23] was used for the analysis of the experimental results in this investigation.

The reduction of metal oxide with CO is assumed to be a surface control chemical reaction and the formula is as follows;

$$\phi(X) = 1 - (1 - X)^{1/F_g}$$

While the gaseous diffusion mechanism is;

$$g(X) = X + (1 - X) \ln(1 - X)$$

where, $\phi(X)$ and $g(X)$ are the interfacial chemical reaction and gaseous diffusion control conversion functions respectively, X is the decimal fractional reduction, and F_g is the grain shape factor.

The mathematical formulae for gaseous diffusion, chemical reaction and mixed control were applied. Straight lines were obtained for the interfacial chemical reaction control mechanism by plotting $\phi(X)$ against time which confirms that it is the rate controlling mechanism at the initial stages of reaction for ferrite samples fired at 1,000–1,200 °C as shown in Fig. 7. On applying the formula of the gaseous diffusion control during the initial stages of reaction on the compacts fired at any temperature, the relationship between $\phi(X)$ and t is not a straight line. This confirms that the interfacial chemical reaction is the rate controlling mechanism at the initial stages of reaction. At the final stages, straight lines were obtained if $g(X)$ is plotted against time confirms that for compacts fired at 1,000–1,200 °C, the rate controlling is the gaseous diffusion mechanisms.

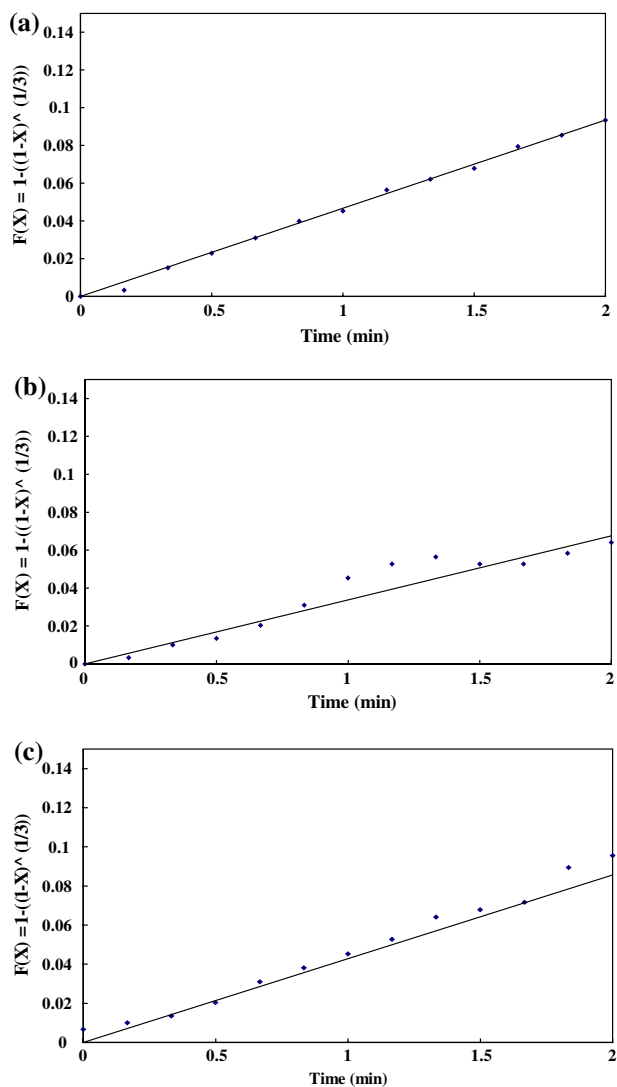


Fig. 7 Application of the interfacial chemical reaction rate control equation at the initial stages of reaction for ferrite powders fired at; (a) 1,000 °C (b) 1,100 °C (c) 1,200 °C

4 Conclusion

The influence of structure changes and firing temperature of ferrite powders on the catalytic oxidation of CO over nanocrystallite $\text{Cu}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ was investigated using advanced quadruple mass gas analyzer system. The different phases formed during firing of ferrite samples were detected using XRD.

The degree of catalytic oxidation of CO was calculated as the conversion extent of CO to CO_2 . The maximum CO conversion was observed for ferrite powders which have

equal amount of Cu^{2+} and Mn^{2+} ($\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$). The high catalytic activity of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ can be attributed to the changes of the valence state of catalytically active components of the ferrite powders.

The CO catalytic oxidation reactions on the surface of nanocrystallite $\text{Cu}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ at different Cu^{2+} and firing temperatures was done by the reduction of the ferrite by CO to the oxygen deficient lower oxide then reoxidation of this phase to the saturated oxygen metal ferrite again. This mechanism of catalytic oxidation reactions was confirmed using thermogravimetric technique. The mathematical formulations indicate that interfacial chemical reaction mechanism is the rate controlling mechanism at the initial stages while gaseous diffusion mechanism is the rate controlling mechanism at the final stages of reaction.

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