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Electronic and catalytic studies on $Co_{1-x}Cu_xMn_2O_4$ for CO oxidation

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Spinels of the composition $Co_{1-x}Cu_xMn_2O_4$ ($x = 0.0, 0.3, 0.5, 0.7$ & 1.0) have been prepared by co-precipitation technique. These were characterized by X-ray diffraction, infra-red spectroscopy, atomic absorption spectroscopy and BET method. The solid state studies such as electrical resistivity, magnetic susceptibility and electron spin resonance have been carried out and attempts have been made to correlate with the catalytic activity of the compounds. The intermediate compositions displayed better catalytic activity than the end compositions for carbon monoxide oxidation due to the phenomena of synergism. Behaviour of the activity pattern has been explained based on cation distribution in tetrahedral (A) and octahedral (B) sites. Crystallographic phase transition is observed from tetragonal to cubic at $x > 0.5$ by substitution of Cobalt with Copper. © *2000 Kluwer Academic Publishers*

1. Introduction

Spinels (AB_2O_4 type) exhibit a variety of applications in electronics, magnetic materials and as catalysts [1, 2]. Complex oxides with a spinel structure are found to be promising catalysts for the oxidation of CO as well as hydrocarbons on account of their better activity and thermal stability as compared to individual oxides [3]. Among known spinels, manganites are less studied, although some authors have shown their high activity and stability in oxidation reactions [4]. The catalytic properties of these oxide spinels can suitably be modified by incorporating different metal ions in the lattice to improve the quality of the materials. The oxidation of CO with the object of reducing air pollution is obviously an important consideration in terms of automobile and industrial emmision control. Carbon monoxide oxidation has been studied over different types of catalysts by many investigators [5–8]. Studies have shown that the non-noble metal containing catalysts such as cobalt and copper are chemically active species for CO oxidation [9, 10]. In the present investigation an attempt has been made to understand the effect of tetrahedral (A) site substitution by copper in the lattice of $CoMn_2O_4$ and to show the comparative catalytic activity of manganites with various cationic compositions prepared by co-precipitation method in the oxidation of CO and their correlation with the physical properties.

2. Experimental procedure

The spinel type manganite compositions $Co_{1-x}Cu_x Mn_2O_4$ were synthesized by a co-precipitation technique as discussed earlier [11, 12]. The required metal nitrates and acetates (A.R. grade) were taken in a stoichiometric proportion, dissolved in distilled water and precipitated using sodium hydroxide solution. The precipitate obtained was digested in a water bath. The resultant precipitated hydroxide mixture was subjected to oxidation using H_2O_2. The precipitate was then washed, filtered and dried at 353 K. The dried precipitate was homogenised well in an agate mortar and further heated in air at around 1000 K for 10 h.

The solid compositions prepared by co-precipitation method were characterized by employing X-ray diffraction method (Philips XRD PW 1820) using Cu K_α, filtered through Ni absorber and infrared spectroscopy (IR). IR spectra were recorded on a Shimadzu FTIR instrument, model 8101A. The sodium contamination in the spinels prepared by co-precipitation method using sodium hydroxide was found by employing atomic absorption spectroscopy (AAS). The total BET surface areas were measured using BET nitrogen adsorption method (ANYGAS Version 2.10). The electrical conductivity measurements were carried out by two probe conductivity cell in the temperature range of 300 to 723 K. The magnetic susceptibility (χ_g) in air of the spinels were determined by Guoy method at room temperature employing a field of the order of 10,000 gauss and using $Hg[Co(SCN)_4]$ as a standard material. The ESR spectra were taken at the X-band on a varian E-112 Spectrophotometer at 298 ± 1 K at a field strength of 3220 gauss. The sample was mounted in a quartz tube and TCNE was used as a field calibrant taking its g-value as 2.00277, spectroscopic splitting factor 'g' was obtained from the relation $\mu = -g\beta s$ were 'μ' is the magnetic movement, 'β' is the Bohr Magneton, 'g' the gyromagnetic ratio and 's' is the spin of electron.

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CO oxidation was studied using oxygen in nitrogen with a continuous flow, fixed bed quartz reactor, by placing 1 g of the catalyst powder in between quartz wool plugs. The catalytic activity was determined using a feed gas composition of 5% CO and 5% O_2 in nitrogen. The individual gas flow rates were controlled using flow meters and precision needle valves. The feed gases and the products were analyzed employing an on line gas chromatograph with a molecular sieve 13X column and H_2 as a carrier gas. The CO was prepared by heating formic acid with conc. H_2SO_4, further purified by passing through alkali and molecular sieve traps to remove the impurities such as carbon dioxide and moisture. The nitrogen and oxygen gases were used from pure commercial cylinders.

3. Results and discussion

The sodium contamination was estimated using an AAS and was found to be in the range of 0.3% to 0.4% by weight. Surface areas obtained by the BET nitrogen adsorption method were found from 4.3 to 7.8 m^2/g for these compositions.

3.1. X-ray analysis

The compositions prepared by co-precipitation method were characterized by recording the X-ray diffractograms. The d_{hkl} and 2θ values obtained were compared with the values reported in the literature (JCPDS data file) and found to be monophasic. Since the d_{hkl} value of the intermediate compositions are not reported in the literature, the values were compared with the end compositions namely $CoMn_2O_4$ and $CuMn_2O_4$.

On account of higher sensitivity of $CuMn_2O_4$ to thermal treatment, some of the authors [13, 14] could not obtained a pure sample of this compound. Some others [15, 16] claimed to have obtained it in a cubic phase and only one author [17] could synthesize it in a tetragonal phase. However our results of X-ray analysis after comparison with the values reported in the JCPDS data file have indicated that $CuMn_2O_4$ is a cubic spinel whereas $CoMn_2O_4$ crystallizes in a tetragonal form which is in accordance with the earlier report [18].

Some of the earlier studies [19] have shown that Cu^{+2} has the strongest square (dsp^2) bond forming power among metals of the first transition series and is expected to occupy an octahedral site. The X-ray studies of Zaslavaski *et al.* [20] observed that $CuMn_2O_4$ is not the normal spinel but partially inverted with an inversion parameter 'λ' within the limits $0.67 \leq \lambda \leq 1$. It was observed by Kshirsagar and Biswas [21] that for a $CoMn_2O_4 : CuMn_2O_4$ system there is a transition from tetragonal to cubic form at 53% $CuMn_2O_4$. This study shows that with increase in the concentration of $CuMn_2O_4$ the tetragonality decreases and symmetry becomes cubic in the range of $x > 0.5$.

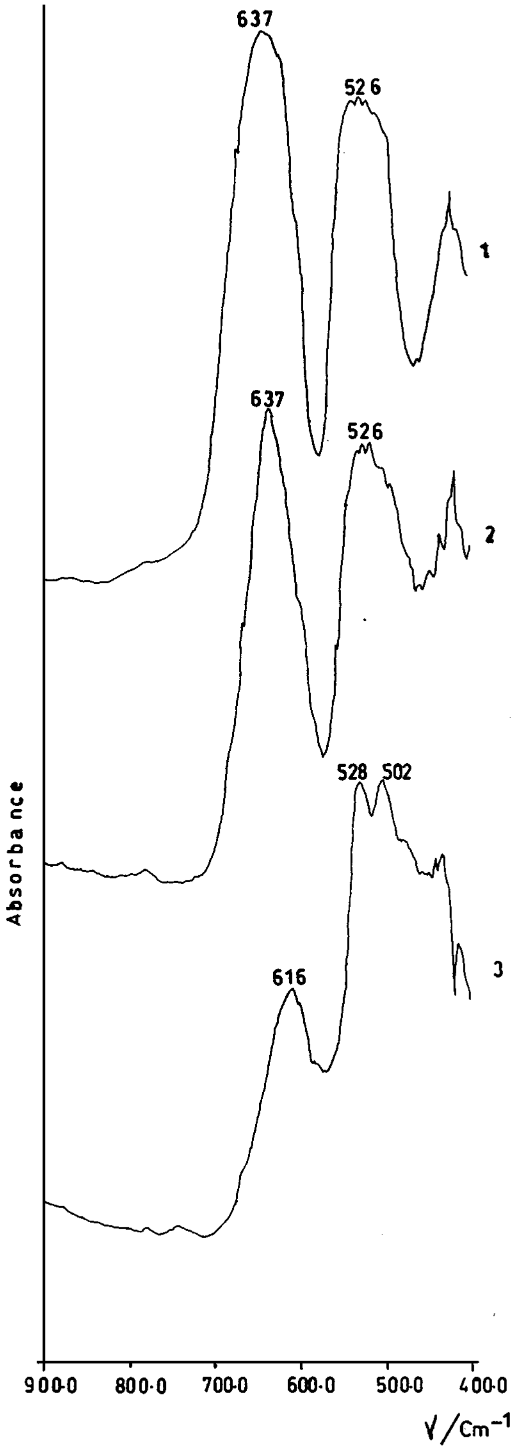

Figure 1 The IR spectra of spinels: 1. $CoMn_2O_4$, 2. $Co_{0.5}Cu_{0.5}Mn_2O_4$ and 3. $CuMn_2O_4$.

3.2. IR analysis

The spinel structure is known to be characterized by IR spectra in the region 700 to 400 cm^{-1} [22]. In the IR spectra of spinels two absorption bands were observed in the 700 to 400 cm^{-1} region corresponding to the stretching vibration of metal oxygen bond as shown in Fig. 1. The short wave band has been assigned to the vibration of metal atom (A) in the tetrahedral environment of oxygen atom (M-O) and the long wave band is assigned to the vibration of metal atom (B) in the octahedral site of the spinel [10]. The difference in the position of the bands in the IR spectra of different samples are due to the mutual interaction of metal ions (A and B) occuring in tetrahedral (Td) and octahedral (Oh) sublattices respectively. With the rise in calcination temperature the simple oxides diffuses resulting

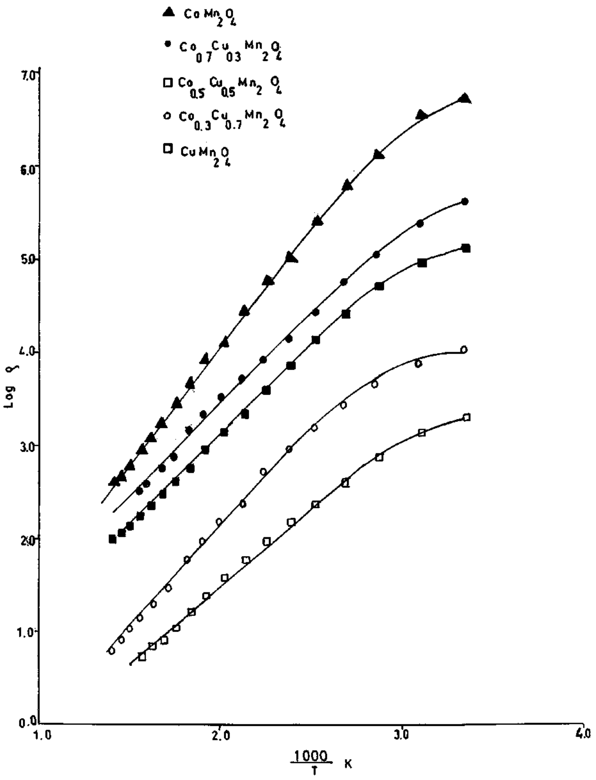

Figure 2 Variation of electrical resistivity of $Co_{1-x}Cu_xMn_2O_4$ with temperature.

in the formation of complex oxides. Thus the intensities of the bands in the IR spectrum corresponding to spinel structure increases and the bands corresponding to simple oxides disappears. However in case of three component oxides two prominent peaks were observed in the region 700 to 400 cm^{-1} corresponding to tetrahedral and ocahedral sites respectively. The shoulder peaks may correspond to various metal ions in Td and Oh sites.

3.3. Electrical and magnetic studies

Electrical resistivity of different spinels were measured using two probe method from room temperature (R.T.) to 723 K. The conductivity of manganites were found to vary in the range 10^2–10^{-11} $ohm^{-1}\,cm^{-1}$ at R.T. as expected for semiconductors. Plot of resistivity vs temperature is shown in Fig. 2 for $Co_{1-x}Cu_xMn_2O_4$. Resistivity decreases linearly with increase in temperature for all the compositions.

Among the different compositions $CoMn_2O_4$ displayed highest resistivity, $CuMn_2O_4$ lowest and medium for intermediate compositions. The resistivity decrease is considerably large beyond $x = 0.5$ which is quite expected on account of excess copper. As B-site cations are responsible for electrical conduction by virtue of site symmetry, the more significant B-B interaction would determined the electrical conduction due to transfer of electrons from B-site Mn^{3+} ions to B-site Mn^{4+} ions as can be explained from the following ionic equation given by Sinha *et al.* [23].

$$Cu^{2+} + Mn^{3+} \rightarrow Cu^{1+} + Mn^{4+} \tag{1}$$

Low resistivity in manganites is explained on the basis of Mn^{3+} - Mn^{4+} ion pair association as reported elsewhere [15, 24–26]. Higher resistivity of $CoMn_2O_4$ is on account of its normal symmetry and a strong tendency of Co^{+2} to occupy tetrahedral site. Further cobalt cannot be so easily reduced unlike copper in $CuMn_2O_4$. Thus the observed high resistivity of $CoMn_2O_4$ can be explained as due to tetragonal stabilization of lattice. This is also supported by the ionic structure given by Yamamoto [27] from neutron diffraction studies.

$$Co^{2+}_{0.84}\ Mn^{2+}_{0.16}\ [Co^{3+}_{0.16}\ Mn^{3+}_{1.84}]\ O^{2-}_4 \tag{2}$$

However a small degree of conductivity in $CoMn_2O_4$ due to Mn^{2+} - Mn^{3+} cannot be neglected which is on account of oxidation of cobalt as shown below.

$$Co^{2+} + Mn^{3+} \rightarrow Co^{3+} + Mn^{2+} \tag{3}$$

High resistivity for compositions with small 'x' value is due to less number of Mn^{3+} - Mn^{4+} ion pairs resulting in the large average distance between equivalent sites available for hopping. Higher conductivity in $CuMn_2O_4$ is attributed to tetrahedrally situated Cu^{2+} - Cu^{1+} ions besides Mn^{3+} - Mn^{4+} ion pairs which has been considered by Kshirsagar [16] with ionic structure conveniently represented as

$$Cu^{2+}_{1-z}\ Cu^{1+}_{z}\ [Mn^{3+}_{2-z}\ Mn^{4+}_{z}]\ O^{2-}_4\quad (0 < Z < 0.1) \tag{4}$$

With increase in copper content in solid solutions the number of Mn^{3+} - Mn^{4+} ion pairs at B-site increases resulting in the corresponding decrease of resistivity which is an inverse function of Mn^{4+} ion concentration.

Bhandage and Keer [1] have proposed the following configuration for $CuMn_2O_4$ based on structural, electrical and magnetic behaviour.

$$Cu^{1+}_{0.6}\ Cu^{2+}_{0.1}\ Mn^{3+}_{0.3}\ [Cu^{2+}_{0.3}\ Mn^{3+}_{1.1}\ Mn^{4+}_{0.6}]\ O^{2-}_4 \tag{5}$$

Our studies are in agreement with the above ionic structure. Based on above ionic configurations (2 & 5) the following cationic distributions are assigned for the intermediate compositions with $x = 0.3, 0.5$ and 0.7 respectively.

$$Co^{2+}_{0.588}\ Mn^{2+}_{0.112}\ Mn^{3+}_{0.09}\ Cu^{1+}_{0.18}\ Cu^{2+}_{0.03}\ [Co^{3+}_{0.112}\ Cu^{2+}_{0.09}\ Mn^{3+}_{1.618}\ Mn^{4+}_{0.18}]\ O^{2-}_4 \tag{6}$$

$$Co^{2+}_{0.42}\ Mn^{2+}_{0.08}\ Mn^{3+}_{0.15}\ Cu^{1+}_{0.3}\ Cu^{2+}_{0.05}\ [Co^{3+}_{0.08}\ Cu^{2+}_{0.15}\ Mn^{3+}_{1.47}\ Mn^{4+}_{0.3}]\ O^{2-}_4 \tag{7}$$

$$Co^{2+}_{0.252}\ Mn^{2+}_{0.048}\ Mn^{3+}_{0.21}\ Cu^{1+}_{0.42}\ Cu^{2+}_{0.07}\ [Co^{3+}_{0.048}\ Cu^{2+}_{0.21}\ Mn^{3+}_{1.322}\ Mn^{4+}_{0.42}]\ O^{2-}_4 \tag{8}$$

TABLE I Magnetic susceptibility data of different spinels

Catalysts	χ_g	μ_{eff} (B.M.)
$CoMn_2O_4$	4.454×10^{-5}	5.0090
$Co_{0.7}Cu_{0.3}Mn_2O_4$	4.675×10^{-5}	5.1470
$Co_{0.5}Cu_{0.5}Mn_2O_4$	5.130×10^{-5}	5.4022
$Co_{0.3}Cu_{0.7}Mn_2O_4$	5.540×10^{-5}	5.6249
$CuMn_2O_4$	6.084×10^{-5}	5.9119

TABLE II ESR data of different spinels

Catalysts	g-Value	Line width (gauss)
$CuMn_2O_4$	1.96	780
$Co_{0.5}Cu_{0.5}Mn_2O_4$	2.21	1440
$CoMn_2O_4$	v.w. signal	—

From over all observation of electrical conductivity data it may be concluded that in the case of composition with $x \leq 0.5$ the conductivity results from Mn^{3+} - Mn^{4+}, Cu^{1+}-Cu^{2+} and Mn^{2+} - Mn^{3+} ion pairs, whereas for $x > 0.5$ conductivity is more dominated by Mn^{3+} - Mn^{4+} and Cu^{1+}-Cu^{2+} ion pairs, due to large concentration of copper.

The magnetic susceptibility of different samples were determined by Guoy balance at room temperature using a field strength of 10,000 gauss. The observed gram susceptibility value at room temperature and magnetic moment values are presented in Table I for $Co_{1-x}Cu_xMn_2O_4$ system. $CuMn_2O_4$ showed lowest grams susceptibility value and highest value displayed by $CuMn_2O_4$. The higher value of magnetic susceptibility for $CuMn_2O_4$ may be due to the presence of copper ions. The presence of Cu^{2+} and Mn^{3+} ions in the spinel which have substantial additional Jahn-Teller stabilization on interaction, results in the formation of ions pairs such as Mn^{3+} - Mn^{4+} along with Cu^{1+} or Mn^{3+} - Mn^{4+} with Cu^{1+} as well as Cu^{2+}. With increase in copper concentration in $Co_{1-x}Cu_xMn_2O_4$ the B-B interaction becomes stronger with increasing Mn^{3+} - Mn^{4+} ion pairs, which facilitates the transfer of electrons there by resulting in an increase of magnetic susceptibility. Formation of such Mn^{3+} - Mn^{4+} ion pairs on account of B-B interaction raises the magnetic susceptibility which is higher in case of $CuMn_2O_4$.

Relative strength of A-site ions in stabilizing tetragonal distortion of the lattice by B-site Mn^{3+} ion is given by Kshirsagar and Biswas [21] as $Zn^{2+} > Mn^{2+} > Co^{2+}$. Thus lower values of magnetic susceptibility for $CoMn_2O_4$ can be explained on the basis of tetragonal stabilization, since magnetic B-B interaction is diluted by decreasing Mn^{3+} - Mn^{4+} ion pairs.

In the series $Co_{1-x}Cu_xMn_2O_4$ as x-value increases symmetry changes from tetragonal to cubic form which get reflected into their magnetic susceptibility values which is also observed earlier [28] for similar such systems ($Zn_{1-x}Cu_xMn_2O_4$). This explains higher magnetic susceptibility for cubic systems like $CuMn_2O_4$ and $NiMn_2O_4$ and lower values of $ZnMn_2O_4$ and $CoMn_2O_4$ which are tetragonal [12, 28] as reported earlier.

The technique of ESR spectroscopy was used as a qualitative tool to get an insight of catalytically active and paramagnetic species such as Cu^{2+}. ESR data of different spinels are presented in Table II. The g-value of ESR spectra for $Co_{1-x}Cu_xMn_2O_4$ are found to decrease with increase in 'x' value. A very weak ESR signal was recorded for $CoMn_2O_4$, however, at $x = 0.5$ ($Co_{0.5}Cu_{0.5}Mn_2O_4$) a peak was recorded with g value of 2.21. Substitution of Cobalt by copper showed an improvement in ESR activity with g value of 1.96 for $CuMn_2O_4$. From ESR studies it is observed that as x-value decreases there is a broadening of the peak resulting in increasing line width. However when x-value tend to zero, a very weak signal was recorded due to absence of copper and on account of strong octahedral site preference of Cu^{2+} ions it is expected to occupy B site in AB_2O_4 type spinel. Presence of considerable amount of Cu^{2+} ions observed on B-site tempted Bhandage and Keer [1] to arrive at the ionic configuration (5) for $CuMn_2O_4$ as shown earlier. Our results of ESR and electrical conductivity are in agreement with the ionic structure thus arrived (5).

3.4. Catalytic oxidation of carbon monoxide

The temperature dependence of CO-conversion studied for different compositions of $Co_{1-x}Cu_xMn_2O_4$ is shown in Fig. 3. Incorporation of copper in the lattice of $CoMn_2O_4$ showed a pronounced change in the catalytic activity for CO oxidation. $CuMn_2O_4$ and $CoMn_2O_4$ showed low conversion rate than the intermediate compositions. The composition with $x = 0.3$ and $x = 0.7$ showed rapid rise in CO conversion with temperature and more than 80% conversion was observed at 478 K. Effect of change in composition on percentage

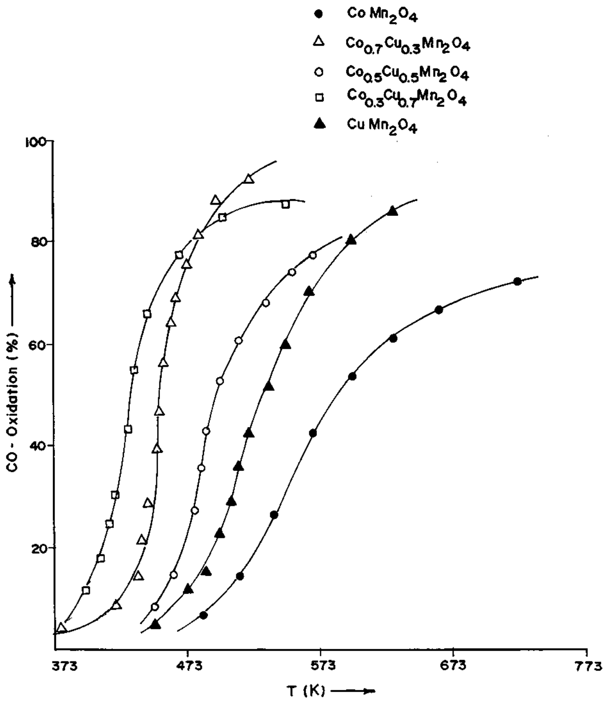

Figure 3 CO conversion as a function of catalyst temperature for $Co_{1-x}Cu_xMn_2O_4$.

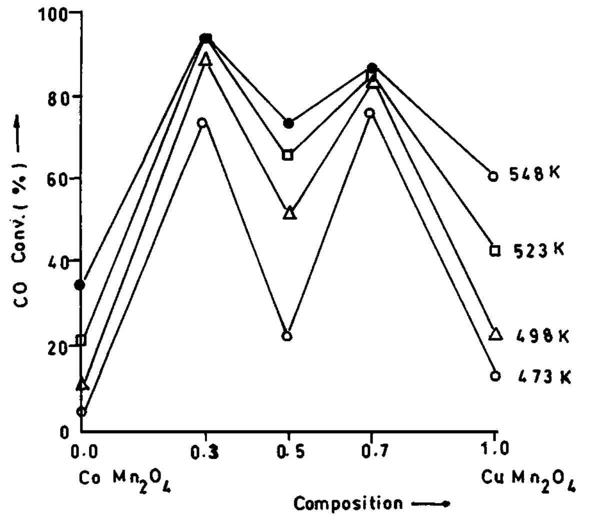

Figure 4 Percentage conversion as a function of catalyst composition at different temperature for the system $Co_{1-x}Cu_xMn_2O_4$.

conversion at different temperatures is shown in Fig. 4. The composition $x = 0.5$ showed lower activity than the other intermediates but comparatively higher than the end compositions. Intermediate compositions $x = 0.3$ and $x = 0.7$ gave higher activity on account of co-operative effect of Co and Cu in the manganite spinels. Data of percentage conversion at various temperatures with corresponding rate of the reaction is shown in Table III. In the series $Co_{1-x}Cu_xMn_2O_4$, $x = 0.3$ composition was found to exhibit highest catalytic activity followed by $x = 0.7 > 0.5 > 1.0 > 0.0$ respectively. The improvement in the catalytic activity in the region of intermediate compositions is on account of the synergistic effect [29] created by breaking the activation energy barrier of the limiting steps. According to Brabers and Setten [30] the octahedral sublattice is mainly occupied by Mn^{3+} (Jahn-Teller ion) which accounts for the tetrahedral deformation of the spinel $CoMn_2O_4$. According to Goodenough and Loeb [31] if cation at the A site forms a strong covalent bond, the corresponding octahedrally cordinated bonds at the B-site becomes weak. The distortion from cubic symmetry to lower symmetry is further explained as due to the formation of covalent bonds. This explains the decrease of CO conversion (Fig. 4) as we go from cubic to tetragonal symmetry. Moreover Cu^{2+} and Mn^{3+} possess same ratio of energetic stabilization of Oh and Td sites as reported elsewhere [32]. According to the studies made by Sinha *et al.* [23] Co^{2+} showed more or less equal affinity for both the types of sites. However according to some of the authors [32] it is more stable on Td site. Since Co^{2+} can be partially oxidized to Co^{3+} in presence of Mn^{3+} according to Equation 3, the resultant Mn^{2+} and Co^{3+} will preferably occupy Td and Oh sites respectively. These studies have tempted us to arrive at ionic structure close to that arrived at by Yamamoto [27] from neutron diffraction studies, represented as in ionic configuration (2), which could satisfactorily explain the low catalytic activity of $CoMn_2O_4$ due to tetragonal stabilization of lattice. Also, observed catalytic activity can be further supported by magnetic susceptibility data which showed lower value of 5.009 BM for $CoMn_2O_4$ due to absence of Mn^{3+}-Mn^{4+} ion pairs which does not result in B-B interaction, in comparison with higher value of 5.912 BM for $CuMn_2O_4$ in the series. Substitution of cobalt by copper showed rise in CO conversion which is maximum at $x = 0.3$ (Fig. 4). Our data of electrical resistivity, ESR and magnetic susceptibility are in agreement with the ionic structure arrived earlier for $CoMn_2O_4$ and $CuMn_2O_4$ as shown in ionic structures (2 & 5). Observed high conductivity of $CuMn_2O_4$ is attributed to Mn^{3+} - Mn^{4+} and Cu^{2+} - Cu^{1+} ion pair association which also accounts for higher magnetic susceptibility. Formation of such ion pair association in unequal proportion is likely to be one of the favourable factor for the catalytic CO oxidation. Formation of ion pair in unequal proportion is on account of mutual interaction between Mn^{3+} and Cu^{2+} thus giving reduced and oxidised species which may also act as active sites for adsorption desorption phenomena as shown in Equation 1. Further the enhancement in ESR activity by added copper also supports the above ionic equation. In absence of copper the electrical conductivity and magnetic susceptibility falls down to minimum on account of reduced electron transfer phenomenon which also reflects on the ESR activity. Hence very weak signal was observed for $CoMn_2O_4$. The electronic interaction among the active sites are considered to be responsible for the catalytic activity. According to some investigators [33] the octahedral sites are exposed exclusively at the surface of spinel oxide. Thus on the basis of above ionic structure the catalytic oxidation of CO can be attributed to Cu^{2+} in copper containing spinels. However according to some of the authors [34] the activity of Cu^{2+} ion is more on Td site than Oh site on account of their susceptibility for reduction. The ionic structures shown above also explains the participation of Cu^{2+}(Td) towards CO oxidation, thus indicating the partial inverse nature of the copper in this spinel, showing the presence of Cu^{2+} on Td as well as on Oh sites. However the oxidation of CO via adsorption on manganese in different oxidation states cannot be ruled out.

TABLE III The reaction rate and the % conversion data at a given temperature for $Co_{1-x}Cu_xMn_2O_4$

Catalysts	Surf. Area (m^2/g)	Reaction temp. (°K)	% CO Conv^n	Rate (molec/$m^2 \cdot s$)
$CoMn_2O_4$	7.76	523	21	1.4148×10^{18}
$Co_{0.7}Cu_{0.3}Mn_2O_4$	6.00	443	27	2.3527×10^{18}
$Co_{0.5}Cu_{0.5}Mn_2O_4$	6.69	473	22	1.7193×10^{18}
$Co_{0.3}Cu_{0.7}Mn_2O_4$	6.5	413	24	1.9303×10^{18}
$CuMn_2O_4$	4.32	495	18	2.1920×10^{18}

Catalytic activity is found to vary with the change in compositions (Fig. 4) based on cation distribution as shown in earlier ionic configurations (2, 5, 6–8). A considerably smaller activity in $CoMn_2O_4$ was observed which is due to octahedrally placed Co^{3+} and Mn^{3+} and there is no Mn^{4+} on Otahedral site which could account for electrical conductivity.

A highest ratio of Oh Mn^{+3}/Mn^{+4} i.e. 8.98 might have resulted in a rapid rise in activity with a small addition of copper (at $x = 0.3$). Further the activity is due to the phenomenon of synergism resulting from the co-operative effect of $CoMn_2O_4$ and $CuMn_2O_4$. Since octahedral sites are exclusively exposed at the surface of the spinel structure, there is a contribution of Co^{+3} and Cu^{+2} for overall activity. However, Cu^{+2} which is more active when present on Td site also results in increasing the activity. The possibility of charge transfer between the newly generated electron exchange couple sites Mn^{+3} - Mn^{+4} and Cu^{+1} - Cu^{+2} might have reduced the active sites of adsorption to some extent.

A fall in the activity in the region of $x = 0.5$ (Fig. 4) is due to further reduction in Mn^{+3}/Mn^{+4} ratio from 8.98 to 4.9. As a consequence of increase in charge transfer between ion pairs such as Mn^{+3}-Mn^{+4}(Oh), Cu^{+1}-Cu^{+2} and Mn^{+2}-Mn^{+3}(Td), the possibility of charge transfer to the adsorbing molecules are reduced and hence decrease in the activity. The incorporation of more copper ($x = 0.7$) decreases Mn^{+3}/Mn^{+4} ratio to 3.2 which is expected to lower the activity, however the added copper removes the tetragonality resulting in crystallographic phase transition to cubic form. Such type of phase transition has been observed to raise the activity. The activity is still expected to be higher but the large amount of copper which result in the formation of more ion pairs, reduces their participation in CO oxidation.

The behaviour in the region $x = 1.0$ with minimum ratio of Mn^{+3}/Mn^{+4} i.e. 1.81 is due to generation of excess electron exchange couple sites, hence fall in activity is observed for $CuMn_2O_4$ (Fig. 4). The activities of intermediate compositions are found to be greater than the end compositions i.e. $CoMn_2O_4$ or $CuMn_2O_4$ with their corresponding Mn^{+3}/Mn^{+4} ratio as 1.84 and 1.81 respectively.

The interpretation of observed trends in catalytic activity of intermediate compositions towards CO oxidation is difficult in the presence of three different metals, since their mutual interaction results in the formation of cations with variable oxidation states such as Cu^{1+}, Cu^{2+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Co^{2+} and Co^{3+}. Besides the large number of factors such as thermodynamic and kinetic parameters, site preference energies and preferential surface enrichment also play a significant role in deciding the overall performance of such catalysts. Some of the earlier reports have shown that at the surface of the catalyst, copper ions are partially reduced by manganese ions, thus causing lower activity of Mn containing mixed oxides [35]. In presence of copper and cobalt the invariable occurrence of manganese give rise to manganese species in different oxidation states. Thus there is variable contribution of Mn ions towards CO oxidation for different compositions.

4. Conclusion

The study of the catalytic activity on substituted $CoMn_2O_4$ in which cobalt is replaced by copper, has changed the co-ordination of cobalt ions in the spinel network, leading to a change in the rate of CO oxidation reaction. At $x = 0.3$, higher catalytic activity is due to the Oh Mn^{+3}/Mn^{+4} ratio i.e. 8.96 as per the ionic configuration. Intermediate compositions exhibited better catalytic activity then the end compositions which is further on account of the phenomenon of synergism. Improvement in the catalytic activity observed in the region of intermediate compositions ($x > 0.5$) suggests that the crystallographic phase ransition is also the factor responsible for CO conversion. The electrical resistivity of different compounds were found to depend on the ion pair association (Mn^{+3}-Mn^{+4}) occupying the Oh site of the spinel. The observed decrease in resistivity with increase in copper is on account of more Mn^{+3}-Mn^{+4} ion pairs, besides Cu^{+1}-Cu^{+2} and Mn^{+2}-Mn^{+3} ion pairs which are due to the interaction between Mn^{+3}, Co^{+2} and Cu^{+2}. Magnetic susceptibility studies showed higher value for cubic system ($CuMnO_4$) and lower value for tetragonal system ($CoMnO_4$). Higher magnetic susceptibility is attributed to the Mn^{+3}-Mn^{+4} ion pairs resulting from Jahn-Teller stabilization of Cu^{+2} and Mn^{+3} ions. Resistivity behaviour, electron spin resonance and magnetic susceptibility studies are in agreement with the ionic configuration and site preference of metal ions which favoured the observed catalytic activity.

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References

1. G. T. BHANDAGE and H. V. KEER, *J. Phys. C, Solid State Phys.* **8** (1975) 501.
2. K. R. KRISHNAMURTHY, B. VISHWANATHAN and M. V. C. SASTRI, *Indian J. Chem. A* **15** (1977) 205.
3. A. K. NEYESTANAKI and L. E. LINDFORS, *Combust. Sci. Tenhnol.* **97**(1/3) (1994) 121.
4. L. YA. MARGOLIS and O. V. KRYLOV, *Problemi Kinetiki I Kataliza* (Problems of kinetics and catalysis) **187** (1981) 120.
5. K. S. R. C. MURTHY and J. GHOSE, *J. Catal.* **147** (1994) 171.
6. YU V. TYURKIN, E. N. LUZHKOVA, N. PIROGOVA and L. A. CHISALOV, *Catal. Today* **33** (1997) 191.
7. F. H. M. DEKKER, M. C. DEKKER, A. BLIEK, F. KAPTEIJN and J. A. MOULIJN, *ibid.* **20** (1994) 409.
8. B. VISHWANATHAN and S. SUSAN GEORGE, *Indian J. Technol.* **22** (1984) 388.
9. B. VISHWANATHAN, K. R. KRISHNAMURTHY and M. V. C. SASTRI, *J. Res. Inst. Catal.* (Hokkaido Univ.) **27** (1979) 79.
10. G. N. PIROGOVA, N. M. PANICH, R. I. KOROSTELEVA and YU. V. VORONIN, *Russ. Chem. Bull.* **45**(11) (1996) 2525.
11. B. A. MULLA and V. S. DARSHANE, *Indian J. Chem. A* **22** (1983) 143.
12. S. M. GURAV and A. V. SALKER, *Indian J. Chem. A.* **38** (1999) 136.
13. G. BLASSE, *J. Phys. Chem. Solids* **27** (1966) 383.
14. G. RIENACKER and K. WERNER, *Z. Anorg. Chem.* **327** (1964) 275.
15. A. P. B. SINHA, N. R. SANJANA and A. B. BISWAS, *J. Phys. Chem.* **62** (1958) 191.

16. S. T. KSHIRSAGAR, *J. Phys. Soc. Japan* **27** (1969) 1164.
17. R. BUHL, *J. Phys. Chem. Solids* **30** (1969) 805.
18. N. YAMAMOTO, S. KAWANO, N. ACHIWA, M. KIYAMA and T. TAKADA, *Japn. J. Appl. Phys*. **12**(11) (1973) 1830.
19. J. B. GOODENOUGH and A. L. LOEB, *Phys. Rev*. **98** (1955) 398.
20. A. I. ZASLAVSKII, Z. V. KARACHENTSVA and A. I. ZHARINOVA, *Soviet Phys. Crystallogr*. **7** (1963) 680.
21. S. T. KSHIRSAGAR and A. B. BISWAS, *J. Phys. Chem. Solids* **28** 1493 (1967).
22. T. V. ANDRUSHKEVICH, G. K. BORESKOV, V. V. POPOVSKII, L. M. PLYASOVA, L. G. KARAKCHIEV and A. A. OSTAN'KOVICH, *Kinet. Katal*. **9** (1968) 1244.
23. A. P. B. SINHA, N. R. SANJANA and A. B. BISWAS, *Acta. Cryst*. **10** (1957) 439.
24. J. B. GOODENOUGH, *J. Phys. Radium* (Paris) **20** (1959) 155.
25. A. P. B. SINHA and K. P. SINHA, *Indian J. Pure Appl. Phys*. **1** (1963) 286.
26. D. B. GHARE, A. P. B. SINHA and A. L. SINGH, *J. Mat. Sci*. **3** (1968) 389.
27. N. YAMAMOTO, S. KAWANO and N. ACHIWA, *Funtai Oyobi Funmatsuyakin* **30**(2) (1983) 48.
28. S. M. GURAV and A. V. SALKER, *Indian J. Chem. Technol.* **5** (1998) 286.
29. J. LAINE, J. BRITO, F. SEVERINO, G. CASTRO, P. TACCONI, S. YUNES and J. CRUZ, *Catal. Lett*. **5** (1990) 45.
30. V. A. M. BRABERS and F. V. SETTEN, *J. Phys. D, Appl. Phys*. **16L** (1983) 169.
31. J. B. GOODENOUGH and A. L. LOEB, *Phys. Rev*. **98** (1955) 391.
32. J. D. DUNITZ and L. E. ORGEL, *J. Phys. Chem. Solids* **3** (1957) 318.
33. J. P. JACOB, A. MATHA, J. G. H. REINTJES, J. DRIMAL, V. PONEC and H. H. BRONGERSMA, *J. Catal.* **147** (1994) 294.
34. J. GHOSE and K. S. R. C. MURTHY, *J. Catal*. **162** (1996) 359.
35. B. L. YANG, S. F. CHAN, W. S. CHANG and Y. Z. CHEN, *ibid*. **130** (1991) 52.

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