

Electrical, magnetic and catalytic carbon monoxide oxidation studies on $Zn_{1-x}Cu_xMn_2O_4$ system

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Kinetics of carbon monoxide oxidation over $Zn_{1-x}Cu_xMn_2O_4$ ($x = 0.0, 0.3, 0.5, 0.7, 1.0$) prepared by co-precipitation method has been studied in the temperature range 373-673 K. Results have been discussed in the light of X-ray powder diffraction, atomic absorption spectrometry, gas chromatography, electrical conductivity, magnetic susceptibility, electron spin resonance and surface area measurements. Higher activity of intermediate compositions is due to the co-operative effect of two different A-site metal ions and crystallographic phase transition.

Many spinels have found potential applications such as semiconductors, magnetic materials in addition to being good catalysts^{1,2}. These oxidic spinels have distinct structural features which play a vital role in determining their electrical, magnetic and catalytic activities. The study of these system is quite useful in understanding the fundamental and technological aspects to provide a rational basis for the catalyst selection. There is a growing demand for the pollution control catalysts either for industries or for the automobiles to have effective, stable and economical catalysts. Many investigators have studied carbon monoxide (CO) oxidation over different types of catalysts³⁻⁸. Although this reaction has the importance of its own, it has been used as a model reaction to tests the catalysts. Investigations of catalytic activity of spinels showed that they are better catalysts in view of their activity and stability as compared with individual oxides^{9,10}. In the present investigation electrical, magnetic and catalytic studies over $Zn_{1-x}Cu_xMn_2O_4$ synthesized by co-precipitation method are presented.

Experimental Procedure

The solid catalysts of compositions $Zn_{1-x}Cu_xMn_2O_4$, were prepared by co-precipitation technique^{11,12}. The respective metal nitrates and acetates of A. R. grade were taken in stoichiometric proportions and dissolved in distilled water to obtain a clear homogeneous solution. To this NaOH was added with constant stirring till the

precipitation is complete. The precipitate was then digested on a water bath for three hours. The precipitated hydroxides mixture was subjected to oxidation by dropwise addition of 30% H_2O_2 from a burette with continuous stirring. The precipitate was then washed with water, filtered and dried at 353 K. The dried precipitate was homogenised well in a mortar and then heated in a furnace at 973 - 1073 K for 10 h.

The prepared compositions were characterized by employing X-ray powder diffraction method using $Cu K_{\alpha}$, filtered through Ni absorber (Philips XRD PW 1820). The sodium contamination in the spinels prepared by co-precipitation method using NaOH, was found out using an AAS. Surface area of the compositions were measured using BET, nitrogen adsorption method (ANYGAS Version 2.10). Electrical conductivity measurements were carried out by two probe conductivity cell in the temperature range of 300-723 K. The magnetic susceptibility in air of the spinels were determined by Guoy method at room temperature (R.T). A field of the order of 10,000 gauss was employed. Mercury tetrathiocyanatocobaltate ($Hg [Co(SCN)_4]$) was used as a standard material. The ESR spectra were taken at the x-band on a varian E-112 spectrometer at 298 ± 2 K by employing 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) or gyromagnetic ratio was obtained from the relation $\mu = -g\beta s$, where ' μ ' is the magnetic moment, ' β ' the Bohr

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magneton, g the gyromagnetic ratio and s is the spin of electron $+1/2$ or $-1/2$.

Carbon monoxide oxidation by oxygen was studied in a continuous flow, fixed bed glass reactor, in which ~ 1 g of the catalyst powder was supported between glass wool plugs. The catalytic activity was determined using a feed gas composition of 5% CO, 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 analysed employing an on-line gas chromatograph with molecular sieve 13X column and H_2 as a carrier gas. The CO was prepared by standard procedure and was purified by passing through appropriate traps. The N_2 and O_2 gases were used from pure commercial cylinders.

Results and Discussion

The formation of monophasic spinels were checked by recording the X-ray diffractograms of all the samples. 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} of the intermediate compositions are not reported in the literature, the values were compared with the end compositions.

The extent of sodium contamination in the samples, prepared by the co-precipitation method using NaOH, was estimated by AAS and it was found to contain in the range of 0.2% to 0.4% by weight. BET surface areas obtained by using N_2 adsorption method were found in the range of 1.46 to 4.95 m^2/g for these compositions. The various solid state experimental studies such as structural characterization, electrical resistivity, magnetic susceptibility and ESR were carried out.

It is well known that $CuMn_2O_4$ is sensitive to thermal treatment during its preparation. Some of the authors^{13,14} could not obtain a pure sample of this compound. However, a number of workers¹⁵⁻¹⁸ claimed to have obtained it in a cubic phase. On the other hand only Buhl¹⁹ could synthesise it only as a tetragonal phase by calcining at 1213 K and quenching from above 1023 K. Below 1023 K $CuMn_2O_4$ progressively gets transformed into a cubic phase. However the present results of X-ray analysis after comparison with the values reported in JCPDS data file has indicated that $CuMn_2O_4$ is a cubic spinel and $ZnMn_2O_4$ crystallizes into a tetragonal form as per the earlier reports²⁰⁻²³.

Among all the metals in first transition series, Cu^{2+} has the strongest square (dsp^2) bond forming power, it is expected to occupy an octahedral (Oh) site which is also reported by Goodenough and Loeb²⁴. The results of an X-ray powder study by Zaslavski *et al.*²⁵ showed that $CuMn_2O_4$ is not a normal spinel but partially inverted with inversion parameter λ within the limits $0.67 \leq \lambda \leq 1$. It was observed by Kshirsagar and Biswas²⁶ that for $Zn_{1-x}Cu_xMn_2O_4$ there is a transition from tetragonal to cubic form at around $x = 0.8$.

Electrical resistivity

Electrical resistivity (ρ) of the different prepared samples were measured using two probe method at various temperatures from room temperature to 723 K. The conductivities of manganites found to vary in the range 10^2 to 10^{-11} $ohm^{-1} cm^{-1}$ at room temperature as expected for semiconductors. Plot of resistivity (ρ) versus temperature (T) is shown in Fig. 1 for $Zn_{1-x}Cu_xMn_2O_4$. Resistivity is found to

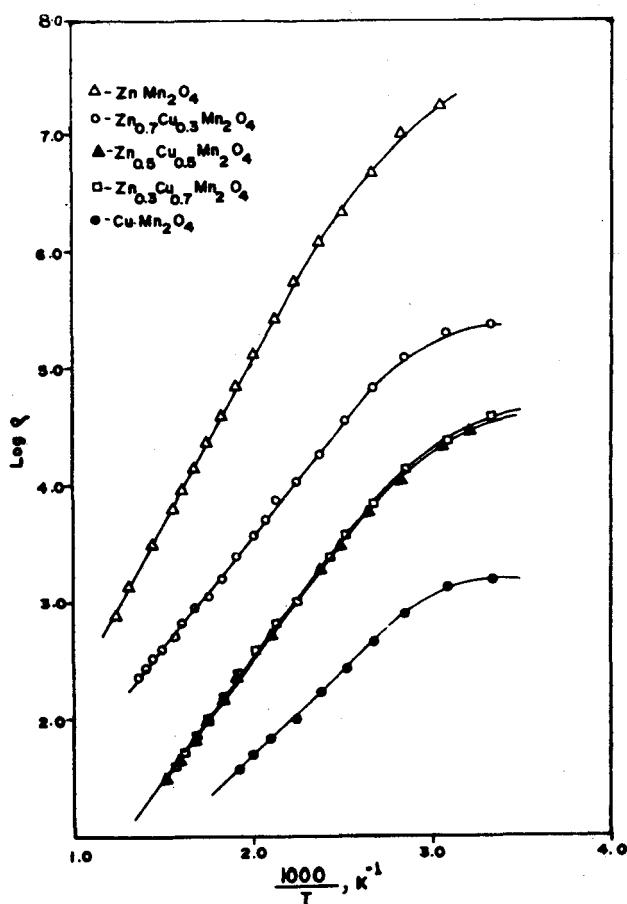


Fig. 1—Variation of electrical resistivity of $Zn_{1-x}Cu_xMn_2O_4$ with temperature

decrease with increase in temperature for all the compositions that were studied for this system.

Resistivity decreases with the increase in copper content in $Zn_{1-x}Cu_xMn_2O_4$ system. The improvement in conductivity is attributed to the copper content rather than zinc at a given temperature. From the literature it is seen that B-site cations are responsible for electrical conduction in spinels by virtue of symmetry. Thus more significant B-B interactions determine the electrical conduction which is as a result of the transfer of electrons from B-site Mn^{3+} ions to B-site Mn^{4+} ions^{27,28}.

In $Zn_{1-x}Cu_xMn_2O_4$ only *p*-type conductivity is likely to be observed throughout the series, since $ZnMn_2O_4$ and $CuMn_2O_4$ are being reported as *p*-type^{16,29}. Resistivity versus temperature plot show a linear variation for all the compositions as observed by Kshirsagar¹⁶ as well as Bhandage and Keer³⁰. It is observed that there is improvement in conductivity at $x = 0.5$ over $x = 0.7$. Similar observations were also made by Larson *et al.*²⁷ for *n-p* type semiconductors.

The observed conductivity in manganites could be explained on the basis of Mn^{4+} - Mn^{3+} ion pair association which is in agreement with reports of many authors^{15,31-34}. The result can be easily explained on the basis of an electron transfer process shown by Sinha *et al.*³⁵ as

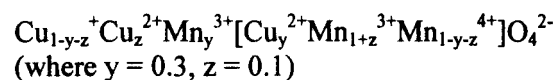


Comparatively high resistivity was observed for compositions with small *x*-value which may be due to low concentration of Mn^{3+} - Mn^{4+} ion pairs resulting in the large average distance between equivalent sites available for hopping. With increase in copper content in solid solution the number of 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.

Higher conductivity of $CuMn_2O_4$ can be attributed to the tetrahedrally located Cu^{2+} and Cu^{+} ions besides Mn^{3+} - Mn^{4+} ion pairs which have been considered by Kshirsagar¹⁶ with the ionic structure conveniently represented as



Bhandage and Keer¹ have proposed the following configuration for $CuMn_2O_4$ based on structural, electrical and magnetic behaviour.



With the increase in *x*-value resistivity is found to decrease for variable compositions at constant temperature. Decrease in resistivity with increase in copper content is known due to Mn^{3+} - Mn^{4+} ion pairs. $ZnMn_2O_4$ is expected to exhibit relatively higher resistivity on account of its normal symmetry and strong tendency to occupy tetrahedral site, further Zn cannot be so easily reduced unlike copper in $CuMn_2O_4$. Thus the observed high resistivity of $ZnMn_2O_4$ can be explained as due to tetragonal symmetry, which is in agreement with the earlier reports²⁷.

Magnetic susceptibility

The magnetic susceptibility (χ) of different compounds were determined by Guoy balance at room temperature, using a field strength of 10,000 gauss. The observed gram susceptibility values at room temperature and magnetic moment values are presented in Table 1 for $Zn_{1-x}Cu_xMn_2O_4$ system.

The higher value of magnetic susceptibility for $CuMn_2O_4$ may be due to copper ions present in the system. The presence of Cu^{2+} and Mn^{3+} ions in the spinel which have substantial additional Jahn-Teller stabilisation on interaction, results in the formation of ion pairs such as Mn^{3+} - Mn^{4+} along with Cu^{+} or Mn^{3+} - Mn^{4+} with Cu^{+} as well as Cu^{2+} . Formation of Mn^{3+} - Mn^{4+} accounts for the higher magnetic susceptibility which is observed for different compositions containing higher copper

Table 1—Magnetic susceptibility and ESR data of different compositions

Catalysts	χ_g	μ_{eff} (B.M.)	g-Value	Line width (gauss)
$ZnMn_2O_4$	3.988×10^{-5}	4.8048	2.7231	1080
$Zn_{0.7}Cu_{0.3}Mn_2O_4$	4.552×10^{-5}	5.1274	1.9889	1015
$Zn_{0.5}Cu_{0.5}Mn_2O_4$	5.0623×10^{-5}	5.4031	1.9723	1310
$Zn_{0.3}Cu_{0.7}Mn_2O_4$	5.446×10^{-5}	5.5998	1.9675	660
$CuMn_2O_4$	6.084×10^{-5}	5.9119	1.9570	780

content. With increase in Cu concentration in $Zn_{1-x}Cu_xMn_2O_4$, B-B interaction becomes stronger with increasing $Mn^{3+}-Mn^{4+}$ ion pairs, which facilitates the transfer of electrons thereby resulting in a increase of magnetic susceptibility. Relative strength of A-site ions in stabilizing tetragonal distortion of the lattice by B-site Mn^{3+} ion is given by Kshirsagar and Biswas²⁶ as $Zn^{2+} > Mn^{2+}$. A-site Zn^{2+} stabilizes the tetragonal distortion more strongly. Thus lower values of magnetic susceptibility for $ZnMn_2O_4$ can be explained on the basis of tetragonal stabilisation.

In $Zn_{1-x}Cu_xMn_2O_4$ as x -value increases, symmetry changes from tetragonal to cubic form, which gets reflected into their magnetic susceptibility values. This explains higher magnetic susceptibilities for cubic systems like $CuMn_2O_4$ and lower values for $ZnMn_2O_4$ which is tetragonal.

ESR studies

ESR technique was used as a qualitative tool for identification of paramagnetic and catalytically active species such as Cu^{2+} ions. ESR data of different spinels is presented in Table 1. The g -values of ESR spectra for $Zn_{1-x}Cu_xMn_2O_4$ gradually decreases with increase in x -value. As the manganese content is constant throughout the series the variation in g -value may be due to addition of copper.

Results of ESR obtained for $Zn_{1-x}Cu_xMn_2O_4$ are also in consistent with the report¹. There is a large variation in g -value 2.7231 for $ZnMn_2O_4$ and g -value around 2.00 for other compositions. The observed variation in g -value is due to incorporation of Cu in $ZnMn_2O_4$. In $ZnMn_2O_4$ the broad ESR peak is observed with g -value much higher than copper containing compositions. It is also found that the line width for the composition with $x < 0.7$ is more than 1000 gauss whereas for the composition with $x > 0.7$ it is around 700 gauss. The broadening of line width for $x = 0.0, 0.3$ and 0.5 may be due to several factors such as short spin relaxation time, spin-spin interaction, concentration of Zn^{2+} ions and structural configuration which is tetrahedral for $x < 0.7$ and cubic for $x > 0.7$.

Catalytic oxidation of carbon monoxide

The transition metal oxide spinels provide an excellent base for correlating catalytic and solid state properties, because they can be well characterised by different techniques. In the present investigation the variation in catalytic activity of

manganite spinels with A-site substitution is being discussed with respect to CO oxidation. Though this reaction is extensively studied over noble metal oxides and other oxide catalysts, it is not well studied over manganite spinels. This reaction is also significant from the point of automobile and industrial exhaust pollution control.

The spinel $Zn_{1-x}Cu_xMn_2O_4$ is tested for CO oxidation and to understand the role played by Zn^{2+} and Cu^{2+} in the catalytic activity. The temperature dependence of CO conversion studied for different compositions is shown in Fig. 2. The fractional conversion of CO (X_{CO}) v/s W/F_{CO} plot for representative samples is presented in Fig. 3. Kinetic parameters derived from Arrhenius plot are summarised in Table 2.

In $Zn_{1-x}Cu_xMn_2O_4$ with increase in copper content the activity of zinc substituted manganite is increased to a marked extent which is quite expected on account of higher activity of Cu^{2+} species. Relatively low activity is exhibited by the end compositions. However, observed rapid rise of CO conversion in the region of $x = 0.3$ to 0.7 , suggests that combination of both the metals must have created a synergistic⁵ effect breaking the activation energy barrier. $ZnMn_2O_4$ and $CuMn_2O_4$ possess higher activation energies as observed from Table 2. Whereas addition of copper to $ZnMn_2O_4$ reduces the activation energy and falls to minimum at $x = 0.7$ giving higher activity. According to

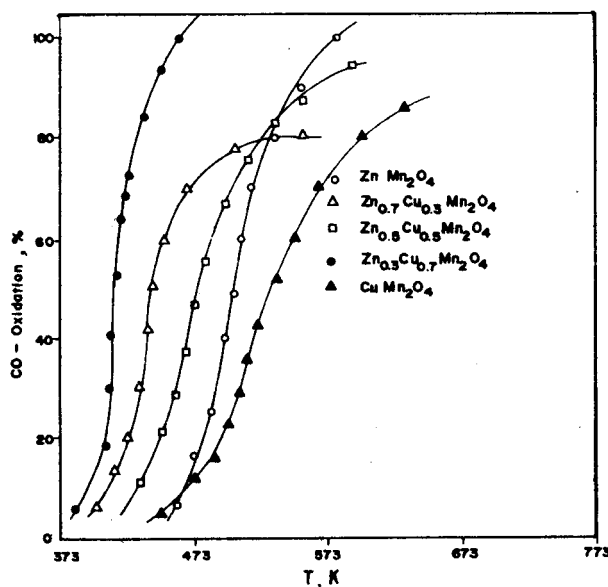


Fig. 2—CO conversion as a function of catalyst temperature for $Zn_{1-x}Cu_xMn_2O_4$

Sinha *et al.*³⁵ the normal arrangement is stabilised by the strong tendency of these ions to form sp^3 bonds (regular or distorted) in the tetrahedral site $Zn^{2+}[Mn^{3+}]_2O_4$. However, a large quantity of $CuMn_2O_4$ (83%) is required to remove the distortion in $ZnMn_2O_4$ as reported by Kshirsagar and Biswas²⁶. Thus a pronounced change in catalytic activity near $x = 0.7$ is attributed to crystallographic phase transition from tetragonal to cubic in the catalyst. Such improvement in the catalytic activity in the region of crystallographic phase transition have been reported elsewhere^{3,36}. This is in agreement with the studies made by Rosenberg *et al.*²⁸ that Jahn-Teller stabilization is dynamic above and static below the transition.

Unexpected decline in CO conversion at $x = 0.5$ can be explained on the basis of electrical conductivity data. The improvement in the conductivity at $x = 0.5$, as explained earlier is attributed to the number of $Mn^{3+}-Mn^{4+}$ ion pair associations in which the formation of Mn^{4+} ion reduces the number of active sites of copper ions (Cu^{2+}). The surface enrichment of manganese over

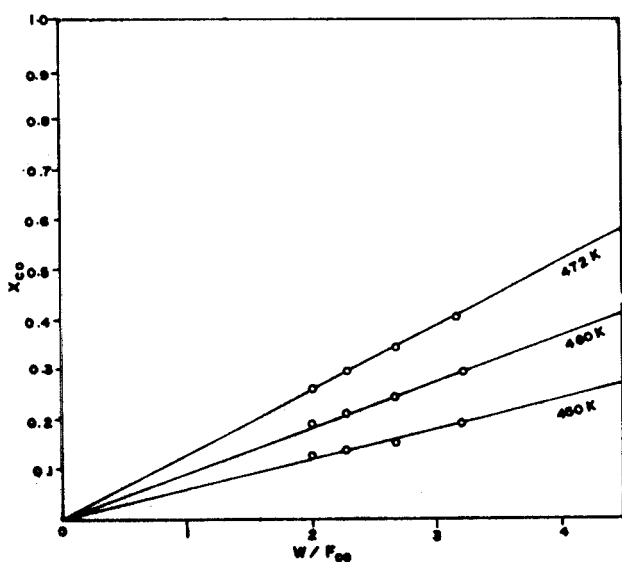


Fig. 3—Resident time plot for the representative sample of $Zn_{0.5}Cu_{0.5}Mn_2O_4$

copper as observed by Yang *et al.*³⁷ and preferential exposure of Oh sites on the surface helps to interpret that the overall activity is reduced to some extent either because active sites of Cu^{2+} are blocked by relatively less active manganese Mn^{3+}/Mn^{4+} or because of reduction of Cu^{2+} by Mn^{3+} giving rise to less active Cu^+ along with Mn^{4+} .

Goodenough and Loeb³⁸ suggested that if the cation at the A-site forms a strong covalent bond, the corresponding octahedrally co-ordinated bonds at B-site become weak, the distortion from cubic symmetry to lower symmetry is further explained as due to the formation of covalent bond. This explains the decrease of CO conversion as we go from cubic to tetragonal symmetry. Moreover Cu^{2+} and Mn^{3+} possess same ratio of energetic stabilization in Oh and Td site as reported elsewhere^{39,40}. Since the partial substitution of Cu by Zn in $CuMn_2O_4$ is likely to produce more of Cu^{2+} on Oh site as Zn prefers only Td site which is in accordance with Jacobs *et al.*⁴¹, such substitution should result in the stabilization of cubic type spinel as observed by Castiglioni *et al.*⁴², thus resulting in the improved catalytic activity towards CO oxidation. The study reveals that the existence of Zn^{2+} and Cu^+ ions play a significant role of adsorption-desorption phenomena in the oxidation reaction of CO. From kinetic studies the energy of activation is found to be lowest for $x = 0.7$ (Table 2) followed by $x = 0.3$ and 0.5 respectively, thus indicating that they possess good catalytic activity for CO oxidation. Relatively higher activation energies observed for $ZnMn_2O_4$ and $CuMn_2O_4$ clearly show that they are catalytically less active. Rate of reaction and frequency factor which are directly proportional to each other cannot be correlated with activation energy, since other parameters such as surface area, temperature etc. also affect the rate and frequency factor.

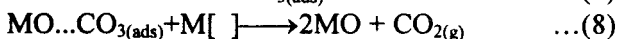
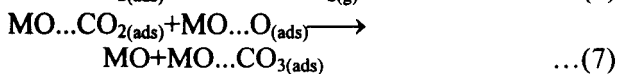
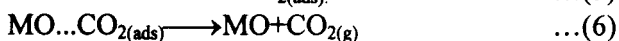
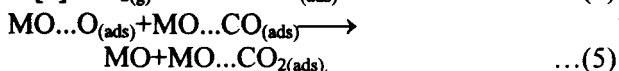
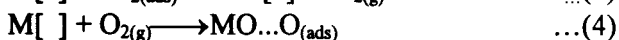
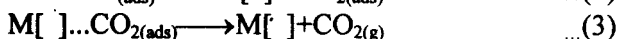
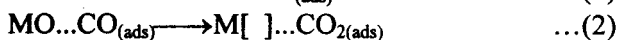
The catalytic carbon monoxide oxidation reaction is observed to be first order with respect to CO and zero order dependence in O_2 for all the

Table 2—Kinetic parameters of CO oxidation over different catalysts

Catalysts	Surf.area(m ² /g)	Temp(K)	Rate(Molec./m ² .s)	E_a (kcal/mol)	Freq.factor(Molec/m ² .s)
$ZnMn_2O_4$	1.46	486	7.0080×10^{18}	10.6080	7.0864×10^{18}
$Zn_{0.7}Cu_{0.3}Mn_2O_4$	2.97	422	3.6000×10^{18}	9.1741	3.6400×10^{18}
$Zn_{0.5}Cu_{0.5}Mn_2O_4$	6.42	450	1.5742×10^{18}	9.8332	1.5917×10^{18}
$Zn_{0.3}Cu_{0.7}Mn_2O_4$	4.95	408	2.1124×10^{18}	8.8878	2.1358×10^{18}
$CuMn_2O_4$	4.32	495	2.1920×10^{18}	12.593	2.2202×10^{18}

compositions. The kinetic studies indicate that adsorption of CO is the rate limiting step. The electrical conductivity data suggests that oxygen adsorption as O^- species is fast and reversible. Such adsorption is found to occur far more extensively on p -type oxides than on n -type oxides.

Many investigators have proposed the reaction mechanism for CO oxidation by oxygen. We propose the reaction mechanism based on earlier data and on our experimental data. Reaction is presumed to proceed by Langmuir-Hinshelwood type mechanism. However there are many reports that reaction also proceeds by Eley-Rideal type mechanism. The proposed reaction mechanism is as follows :



MO indicate oxidic active site of the spinel catalyst and $M[]$ is the reduced active site of catalyst.

In reaction (1) carbon monoxide gets adsorbed on metal oxide by transfer of electron from carbon atom of CO to metal ion M of oxide resulting in the formation of chemisorbed species. In the second step chemisorbed CO species give rise to chemisorbed CO_2 at reduced metal site with anion vacancy. Partially bonded CO_2 gets desorbed leaving reduced metal on the lattice, which subsequently takes up oxygen from the gas phase forming chemisorbed oxygen on MO as shown in the reaction (4). Resultant chemisorbed species may interact with the reactive species produced in reaction (1), forming normal metal oxide as well as metal oxide with adsorbed CO_2 . Adsorbed CO_2 species on metal oxide being unstable at higher temperature, undergoes dissociation to regenerate MO and leaving CO_2 in the gas phase. Chemisorbed species produced in reaction (4) and reaction (5) may also interact to yield carbonate type adsorbed species at MO site which subsequently can react with reduced metal site to finally give metal oxide and carbon dioxide. The above reaction mechanism is in agreement with

many investigations^{29,43-46} in some form or the other.

Conclusion

In $Zn_{1-x}Cu_xMn_2O_4$ the composition with $x = 0.7$ gave maximum catalytic activity. The intermediate compositions were found to be more active than the end compositions due to the phenomena of synergism. Electrical resistivity of different compounds were found to depend on the metal ions occupying the octahedral site of the spinel. Magnetic susceptibility studies showed higher values for cubic system ($CuMn_2O_4$) and lower value for tetragonal system ($ZnMn_2O_4$). Higher magnetic susceptibility of spinel is attributed to Mn^{4+} - Mn^{3+} ion pairs resulting from the Jahn-Teller stabilization of Cu^{2+} and Mn^{3+} ions.

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