X-Ray, Transport, Magnetic, Mössbauer and Catalytic Studies of the System $Zn_{1-x}Cu_xMnFeO_a$

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The system $Zn_{1-x} Cu_x MnFeO_4$ has been studied with a view to investigating the cation distribution, transport and magnetic properties and to correlate the physical properties of oxidic spinels with their catalytic behaviour in benzyl alcohol decomposition. The system was found to be tetragonal in the range $0.0 \le x \le 0.2$ and cubic in the range $0.4 \le x \le 1.0$. The activation energy values of electronic conduction varied between 56.69 and 13.01 kJ mol⁻¹. Thermoelectric power measurements indicated p-type semiconducting nature for all the compounds up to 600 K. Mössbauer studies indicated the ferrimagnetic nature of compounds with $x \ge 0.8$ while the rest of the compositions indicated quadrupole doublets. Catalytic behaviour of the catalysts prepared was investigated for the decomposition of benzyl alcohol in the temperature range 473–673 K. A good correlation could be established between cation distribution, transport, magnetic nature and catalytic behaviour.

Binary and ternary oxides crystallizing with spinel and perovskite structures exhibit catalytic behaviour.¹⁻³ In recent years copper-based catalysts have attained considerable importance owing to their selective properties in the reactions involving hydrogen.⁴ However, individual metal oxides lose their catalytic activity rapidly owing to aging and formation of coke over the surface. The spinel lattice imparts extra stability to the catalyst under various reaction conditions so that these systems have sustained activities for longer periods.⁵

The oxidic spinel containing Cu, Mn and Fe has aroused considerable interest with regard to valency and site distribution. Many worker using different techniques such as X-ray diffraction (XRD), electrical transport and Mössbauer spectroscopy have tried to resolve the problem of cation distribution. Mande and Kulkarni⁶ have suggested the ionic configuration of CuMnFeO₄ as Fe^{3+} [Cu²⁺Mn³⁺]O₄²⁻ on the basis of X-ray absorption studies which is supported by Mathur et al.7 on the basis of Mössbauer studies. However, Teliar et al.8 have suggested the configuration of the compound as, $Fe_{0.85}^{3+}Cu_{0.15}^{1+}[Fe_{0.15}^{3+}Cu_{0.85}^{2+}Mn_{0.85}^{3+}Mn_{0.15}^{4+}]O_4^{2-}$. We have investigated the system $Zn_{1-x}Cu_xMnFeO_4$ with a view to determining the effect of substitution on the structural, transport and magnetic properties of the system and its subsequent effect on the catalytic behaviour towards alcohol decomposition.

Experimental

Preparation of Catalysts

The catalysts of different compositions have been synthesized by a coprecipitation technique using 10% NaOH at a pH of 9.0–9.5. The starting materials were the sulfates (BDH, AR). The hydroxides were oxidized at 363 K with 30% H_2O_2 with constant stirring. The precipitates were digested on a waterbath for 2 h, filtered and washed with doubly distilled water to free them from excess alkali and SO_4^{2-} ions. The compounds were oven dried and then calcined at 1173 K for 4 h. The formation of a single spinel phase was ascertained by XRD and differential thermal analysis (DTA) techniques. The stoichiometries of the compositions were checked by chemical analysis and found to be in agreement with theoretical values (Table 1). To measure electrical conductivity and thermoelectric coefficient pellets were prepared using 2% polyvinyl acetate solution as a binder. Pellets were prepared from the sample (2 g) by applying a pressure of 10 000 psi† and the thickness of the pellets varied between 0.53 and 0.59 cm. Initially, the pellets were heated slowly in air at a rate of 1 K min⁻¹ to remove the binder and then fired at 1173 K, the sintering temperature.

Structural Analysis

X-Ray powder diffraction patterns were recorded on a diffractometer (Siemens D-500 krystalloflex) with microprocessor controller, using nickel-filtered Cu-K α radiation. The X-ray patterns of all the compositions indicated formation of a single spinel phase. To calculate the relative integrated intensity, *I*, of a given (*hkl*) reflection, the following formula¹⁰ was used where the notations have their usual meaning.

$$I_{hkl} = |F_{hkl}|^2 P \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

The atomic scattering powers for the various ions were taken from the literature.¹¹ To determine the cation distribution and its variation with composition, the intensity ratios $(I_{220}/I_{440}, I_{220}/I_{400}, I_{400}/I_{422}, I_{311}/I_{220} \text{ and } I_{311}/I_{222})$ for different possible models of cation distributions were calculated as the reflections 220, 222, 400, 422 and 440 are more sensitive towards cation distribution at both the sites. These were then compared with the observed intensity ratios. The

† 1 psi $\approx 8.894757 \times 10^3$ Pa.

Table 1 Table showing stoichiometry of compounds synthesized by the coprecipitation technique

Zn (%) Cu		(%)	Mn	Mn (%)		Fe (%)		
compound	obs.	theor.	obs.	theor.	obs.	theor.	obs.	theor.
ZnMnFeO ₄ Zn _{0.6} Cu _{0.4} MnFeO ₄ CuMnFeO ₄	27.20 10.95	27.22 10.94	10.60 26.64	10.62 26.66	22.80 22.95 23.05	22.87 22.95 23.10	23.24 23.25 23.39	23.26 23.33 23.43

Table 2Comparison of intensity ratios for Zn_{0.4}Cu_{0.6}FeMnO4

	I ₂₂₀	/I ₄₄₀	I ₂₂₀	/1400	I ₄₀₀	//1422	I ₃₁₁	/// 220	I ₃₁₁	///1222
models of cation distribution	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
(1) $(Zn_{0.4}^2Cu_{0.6}^{2+})$ [Fe ³⁺ Mn ³⁺]		0.83		1.75		0.42		4.2		11.6
(2) $(Zn_{0.4}^{2+}Cu_{0.2}^{1+}Fe_{0.4}^{3+})$ [Fe_{0.6}^{3+}Cu_{0.4}^{2+}Mn_{0.8}^{3+}Mn_{0.2}^{4+}]	_	0.59	_	1.54		1.50	-	3.90		10.90
(3) $(Zn_{0.4}^{2+}Fe_{0.6}^{3+}) [Fe_{0.4}^{3+}Cu_{0.6}^{2+}Mn_{0.8}^{3+}Mn_{0.2}^{4+}]$	0.73	0.74	1.62	1.61	0.45	0.45	3.50	3.48	11.41	11.41
(4) $(Zn_{0.4}^{2+}Fe_{0.6}^{3+})$ [Fe_{0.4}^{3+}Cu_{0.6}^{2+}Mn_{1.0}^{3+}]		0.80		1.50		0.75		3.2		11.7

() = Tetrahedral site; [] = octahedral site.

maximum standard deviation in the observed ratio was ± 0.2 (Table 2).

Transport Studies

D.c. electrical resistivity measurements were carried out from room temperature to 773 K using the two-probe technique. An electric field of 20 V cm⁻¹ was applied across the pellet and resistivity was calculated using the equation $\rho = (\pi d^2/4t)R$ (where d = diameter, t = thickness and R = resistance). The thermoelectric power measurements were carried out after sandwiching a thick pellet between two copper blocks and the temperature difference developed across the pellet was measured using a microvoltmeter. The thermoelectric coefficients were measured from room temperature to 573 K.

Determination of Surface Area

The surface areas of different compositions of the system $Zn_{1-x}Cu_xMnFeO_4$ were determined by conventional BET technique by nitrogen adsorption method at liquid-nitrogen temperature and are listed in Table 6 (see later).

Magnetic Measurements

The magnetic hysteresis at 298 and 77 K for all the compounds was recorded using an a.c. electromagnet type loop tracer.¹² The saturation magnetization (σ_s) was also recorded on a digital multimeter at 298 and 77 K. Initial susceptibility studies were made from 399 to 573 K for the compounds $x \ge 0.6$, using a field of 2 kOe by a double-coil method.¹³ From the plot of χ/χ_i vs. T the Curie temperature (T_c) of the compound was determined.

Mössbauer Studies

Mössbauer measurements were made using a conventional transmission geometry, constant acceleration set-up operating in time mode. A 25 mCi 57 Co source a copper matrix at room temperature was used as the γ -source.

Catalytic Studies

Each composition of the system was studied for its catalytic behaviour towards benzyl alcohol decomposition in the temperature range 473–673 K using a fixed-bed flow reactor. The reactor was 25 cm long (10 mm i.d.) made from Pyrex glass. 3.0 g of the powdered catalyst sample were held between two glass-wool plugs, surrounded by glass beads to facilitate heat exchange. The temperature of the catalyst bed could be measured within ± 1 K with a Cr–Al thermocouple out to the sample through a thermo-well. Benzyl alcohol (Glaxo, Excellar) was distilled before use and checked for its purity by GC. The reactant was fed into the reactor by means of a

motor-driven syringe pump for accurate control and metering of the feed rate. The products were condensed using dry ice-acetone traps. Initially, 20 min was allowed for attainment of steady state before collecting and analysing the products. The products were analysed by means of a chromatograph (Netel QC-Omega) with FID. A standard 10% carbowax 20M (on chromosorb) column was used with nitrogen as a carrier gas (30 dm³ min⁻¹). Throughout the analysis, the column temperature was programmed from 373 to 423 K. The products were further confirmed using authentic samples and GCMS.

The various terms used in the following discussion are defined as, % conversion = [(moles of alcohol reacted)/moles of alcohol passed)] \times 100, % selectivity = [(moles of product formed)/(moles of alcohol consumed)] \times 100.

IR Studies

IR spectra of the catalysts were recorded before and after their use, at room temperature on a spectrophotometer (Perkin-Elmer FTIR-1600) from 2000 to 200 cm⁻¹ using KBr as standard. From the spectra, position of various cations and threshold frequencies were calculated.

Results and Discussion

Structural Analysis

The results of X-ray analysis are summarized in Table 3. The system $Zn_{1-x}Cu_xMnFeO_4$ is tetragonal in the range $0.0 \le x \le 0.2$ and cubic in the range $0.4 \le x \le 1.0$. The values of lattice parameter for $ZnMnFeO_4$ (a = 8.349 Å, c = 8.605 Å) and CuMnFeO₄ (a = 8.40 Å) are in good agreement with the values reported earlier.^{14,15} From Table 3, it can be seen that the lattice constant shows slight increase with increasing copper content in the system. The cation distribution between the two sites in the system, has been arrived at by X-ray intensity calculations. Comparison of the intensity ratios for the compound Zn_{0.6}Cu_{0.4}MnFeO₄ is summarized in Table 2. It is observed that, with the subsequent replacement of Zn^{II} by Cu^{II} ions in the spinel lattice, an equal amount of Fe^{III} ions migrate from the B-site to the A-site. Thus ZnMnFeO₄ has a normal spinel structure with Zn^{2+} ions at tetrahedral sites and Mn^{3+} and Fe^{3+} ions occupying octahedral sites, while CuMnFeO₄ shows an inverse structure with Fe^{3+} at tetrahedral and Cu^{2+} and Mn³⁺ ions at octahedral sites. This is in accordance with the site occupancy data given by Miller.¹⁶

Transport Studies

The room-temperature resistivity values of all the compounds varied between 10^6 and $10^3 \Omega$ cm for different values of x. The electrical resistivity temperature behaviour obeys Wilson's law, $\rho = \rho_0 \exp(\Delta E/kT)$ indicating the semiconducting nature of all the compounds under investigations.

Table 3 Lattice constant, activation energy, thermoelectric emf and cation distribution of the system $Zn_{1-x}Cu_xMnFeO_4$

	lattice parameters							
x	$a/{ m \AA} \pm 0.005$	$c/\text{\AA}$ ± 0.005	activation energy (ΔE) /kJ mol ⁻¹	thermoelectric emf $/\mu V K^{-1}$	cation distribution			
0.0	8.349	8.605	56.69	102.0	(Zn^{2+}) [Fe ³⁺ Mn ³⁺]O ₄ ²⁻			
0.2	8.360	8.605	50.52	95.4	$(Zn_{0.8}^{2+}Fe_{0.2}^{3+})$ [Fe _{0.8} ³⁺ Cu _{0.2} ²⁺ Mn _{0.8} ³⁺ Mn _{0.2} ⁴⁺]O ₄ ²⁻			
0.4	8.370		42.71	66.9	$(Zn_{0.6}^{2+}Fe_{0.4}^{3+})$ [Fe_{0.6}^{3+}Cu_{0.4}^{2+}Mn_{0.8}^{3+}Mn_{0.2}^{4+}]O_4^{2-}			
0.6	8.382		37.31	60.0	$(Zn_{0.4}^{2+}Fe_{0.6}^{3+})$ [Fe_{0.4}^{3+}Cu_{0.6}^{2+}Mn_{0.8}^{3+}Mn_{0.2}^{4+}]O_4^{2-}			
0.8	8.390	—	15.52	53.7	$(Zn_{0.2}^{2+}Fe_{0.8}^{3+})$ [Fe_{0.2}^{3+}Cu_{0.8}^{2+}Mn_{0.8}^{3+}Mn_{0.2}^{4+}]O_4^{2-}			
1.0	8.40		13.01	10.2	$(Fe^{3+}) [Cu^{2+}Mn^{3+}]O_4^{2-}$			

() = Tetrahedral site, [] = octahedral site.

The plot of $\log \rho vs. 10^3/T$ showed no inflection or break indicating stable oxidation states of all the ions over the temperature range studied. The values of activation energy obtained from resistivity plots are listed in Table 3 and are plotted in Fig. 1(*a*). It can be seen that, with the substitution of copper for zinc in the system, the activation energy decreases from 56.69 kJ mol⁻¹ for ZnMnFeO₄ to 13.01 kJ mol⁻¹ for CuMnFeO₄.

The compound CuMnFeO₄ shows fairly low roomtemperature resistivity ($10^3 \Omega$ cm) as compared with ZnMnFeO₄ ($10^6 \Omega$ cm). The low room-temperature resistivity of the former compound can be explained on the basis of a valency exchange mechanism.¹⁷ According to this mechanism, electrical conduction takes place via hopping of electrons between the same cation situated at an octahedral site whose oxidation state differs by unity.

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

The decrease in the activation energy of the system (Table 3) is due to the fact that substitution of Cu^{II} in the lattice of



Fig. 1 Plots of (a) ΔE vs. x; (b) Seebeck coefficient (a) vs. x; (c) % conversion vs. x and (d) % conversion vs. ΔE for the system $Zn_{1-x}Cu_xMnFeO_4$

ZnMnFeO₄ results in an increased number of Cu^{2+}/Cu^{1+} and Mn^{3+}/Mn^{4+} ion pairs and so the conductivity increases and activation energy for the electron conduction decreases. In addition to this, the $Zn^{2+} d^{10}$ orbitals are more contracted than other transition-metal ion d-orbitals. The decreased overlap with the oxygen 2p and the 3d and 4s orbitals of B-site ions has an indirect but appreciable effect on the hopping process at the octahedral site.

Measurements of thermoelectric power indicated all the compounds of the system to be p-type semiconductors. The Seebeck coefficient (α) varied between + 102.0 and + 10.2 μ V K⁻¹ (Table 3) and is plotted in Fig. 1(b). It can be seen that, with increasing copper content in the spinel lattice, the Seebeck coefficient decreases. This is due to the increase in the number of charge carriers with increasing values of x.

Mössbauer Studies

The room-temperature Mössbauer spectra for all the compositions of the system indicated that the compounds with x = 0.8 and 1.0 are magnetically ordered and therefore ferrimagnetic six-line spectra were observed. The other compounds showed quadrupole doublets due to a paramagnetic state. The spetra were fitted with the MOSSFIT program. The Mössbauer spectra for the compounds x = 1.0 and 0.6 are shown in Fig. 2. The ferrimagnetic spectra observed for the compounds x = 0.8 and 1.0 may actually be due to superimposition of two sextets, one due to Fe^{III} ions at an octahedral site and the other to Fe^{III} ions at a tetrahedral site. Since we could not observe any outer-line splitting as observed in the case of the compounds $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{r}Fe_{2-r}O_{4}$,^{18,19} we can say that, all Fe^{III} ions are present at either tetrahedral or octahedral sites. The isomer shift values for the different compositions of the system varied between 0.40 and 0.32 mm s⁻¹ (Table 4) which are typical of Fe^{III} ions in a high-spin state.

IR Studies

All the compounds of the system showed two strong bands v_1 and v_2 at *ca*. 600 and 450 cm⁻¹. A comparatively weaker

Table 4 Mössbauer and magnetic parameters for the system $Zn_{1-x}Cu_xMnFeO_4$

x	$\delta/\mathrm{mm~s^{-1}}$	$\Delta E_{q}/mm \ s^{-1}$	$\sigma_{\rm s}/{\rm emu}~{\rm g}^{-1}$	$T_{\rm c}/{\rm K}$
0.0	0.4	0.61		124
0.2	0.35	0.52		130
0.4	0.33	0.48		230
0.6	0.37	0.44	19.19	305
0.8	0.39	0.12	29.0	379
1.0	0.32	0.08	40.0	472



Fig. 2 Mössbauer spectra of $Zn_{1-x}Cu_xFeMnO_4$ at 298 K for (a) x = 1.0 and (b) x = 0.6

band is observed at *ca.* 310 cm⁻¹. The band positions and threshold frequencies for the different compositions of the system are summarized in Table 5. The threshold frequency is for electronic transitions. It is found to decrease with increasing copper content in the system (Table 5), which is in agreement with the trend observed for the activation energy of conduction (Table 3). The band positions for the compounds x = 0.0 and 1.0 are in agreement with values reported earlier for ferrite spinels.^{20,21}

From systematic experimental IR studies of oxidic spinels using methods of isotopic and isomorphic substitution Preudhomme and Tarte²⁰ have reported that the highfrequency band v_1 has to be assigned to the tetrahedral group, if the cations having highest valency occupy A-sites. Waldron²¹ attributed the high-frequency band v_1 at *ca*. 600 cm⁻¹ to the stretching vibrations of the tetrahedral group and the band at *ca*. 400 cm⁻¹ (v_2) to the vibration of octahedral groups. Therefore, in the compounds investigated, the higher frequency band can be assigned to the tetrahedral stretching vibrations.

With the substitution of Zn^{2+} by Cu^{2+} ions in the spinel lattice the frequencies of stretching vibrations shift from 594.0

Table 5Threshold frequencies and band positions for the differentcompositions of the system $Zn_{1-x}Cu_xMnFeO_4$

	abso	thread-old		
x	v ₁	v ₂	v ₃	frequency
0.0	594.0	461.0	323.0	840.9
0.2	588.0	448.7	309.8	800.0
0.4	587.6	458.0	307.7	798.8
0.6	586.7	459.1	301.2	773.8
0.8	581.1	459.0	309.1	741.1
1.0	579.8	442.0	300.0	741.2

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to 579.8 cm⁻¹ (v_1) and 461.0 to 442.0 cm⁻¹ (v_2). The shift in the v_1 band position may be due to migration of Fe³⁺ ions from B to A sites. This has been observed from X-ray intensity data (Table 2) and Mössbauer studies. The systematic change in the frequency v_2 can be attributed to substitution of Cu²⁺ at the octahedral site and oxidation of Mn³⁺ to Mn⁴⁺ state.

The presence of Fe^{II} ions in the spinel lattice causes a shoulder or splitting.²² However, such splitting of absorption bands is not observed in our system indicating absence of detectable Fe^{II} ions.

Catalytic Studies

Catalytic dehydrogenation is a useful method for the preparation of aldehydes and ketones from primary and secondary alcohols respectively.²³ Benzyl alcohol and its derivatives find extensive use in the perfume industry. A literature survey reveals that benzyl alcohol decomposition has been carried out by several workers using metals, metal oxides and various zeolites.^{24–29} However, no work has been reported where spinels have been used as a catalyst for the decomposition of benzyl alcohol.

Catalytic decomposition of benzyl alcohol yields benzaldehyde and toluene as major products, benzyl benzoate (<5%) and benzene and methanol in small amounts (<1%). Since, the concentrations of these catalysed products are small, they are neglected in our present discussions. The various products formed as a result of catalytic decomposition, may be represented as:

$$C_{6}H_{5}CH_{2}OH \xrightarrow{\text{catalyst}} C_{6}H_{5}CHO + 2H^{*}$$

$$2C_{6}H_{5}CH_{2}OH + O^{*} \longrightarrow C_{6}H_{5}CO_{2}CH_{2}C_{6}H_{5} + H_{2}O^{*}$$

$$C_{6}H_{5}CH_{2}OH + 2H^{*} \longrightarrow C_{6}H_{5}CH_{3} + H_{2}O$$

$$C_{6}H_{5}CH_{2}OH + 2H^{*} \longrightarrow C_{6}H_{6} + CH_{3}OH$$

$$H_{2}O^{*} \longrightarrow H_{2} + O^{*}$$

 $O^* = lattice oxygen$ $H^* = adsorbed hydrogen.$

The catalytic performance data for the decomposition of benzyl alcohol over different compositions of the system $Zn_{1-x}Cu_xMnFeO_4$ are summarized in Table 6. From the table, it is observed that copper-rich catalysts are always more active towards alcohol decomposition than zinc-rich catalysts [Fig. 1(c)]. The increased activity with increasing values of x in the system can be explained in terms of cation distribution, activation energy and charge carriers as follows.

From Fig. 3(*a*), it may be seen that with increasing concentration of Fe^{III} ions at A-sites, benzyl alcohol decomposition (%) increases. This is due to the fact that in the case of ZnMnFeO₄, the A-site is occupied by stable Zn^{II} ions and the catalytic activity is mainly due to the hopping of B-site ions. In CuMnFeO₄, A-sites are occupied by Fe^{III} ions which can hop between +2 and +3 states, thus providing a greater number of adsorption sites for alcohol molecules. Therefore with increasing % of Fe^{III} ions at A-sites in the spinel lattice the activity increases indicating that cation distribution plays an important role in the oxidation of benzyl alcohol. Similar observations have also been reported by Cota *et al.*³⁰ and Onchuku³¹ during the investigations of hydrogen peroxide decomposition over nickel ferrite and copper-nickel ferrite systems, respectively.

The effect of activation energy on the activity of spinel is summarized in Fig. 1(d). It can be seen that with decrease in activation energy decomposition of benzyl alcohol increases. This is due to the fact that catalysis involves transfer of

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Table 6 Catalytic performance data for the decomposition of benzyl alcohol over the different compositions of the system $Zn_{1-x}Cu_xMnFeO_4$

x	catalyst bed temp./K	conv. (%)	benzaldehyde selectivity (%)	toluene selectivity (%)	BET surface area/m ² g ⁻¹
0.0	473	9.6	91.0	1.4	7.5
	523	33.7	85.5	4.2	
	573	40.5	88.8	9.0	
	623	65.5	87.0	10.0	
	673	76.0	22.5	10.6	
0.2	473	23.9	90.3	2.3	6.0
	523	40.0	84.6	7.8	
	573	42.6	81.4	9.0	
	623	66.9	50.6	10.3	
	673	77.0	44.8	15.9	
0.4	473	30.0	85.0	5.0	4.9
	523	44.0	72.0	10.0	
	573	51.0	65.0	13.5	
	623	73.0	48.0	16.0	
	673	81.0	42.5	20.4	
0.6	473	38.0	76.0	7.0	2.6
	523	51.0	68.0	13.0	
	573	69.0	60.0	17.0	
	623	79.0	52.0	22.0	
	673	86.0	49.0	26.0	
0.8	473	49.0	67.0	10.0	1.0
	523	58.0	59.0	18.0	
	573	79.0	47.0	25.0	
	623	87.0	44.0	31.0	
	673	93.0	40.0	38.0	
1.0	473	61.0	54.0	15.0	1.0
	523	72.0	49.0	23.0	
	573	85.0	43.0	29.0	
	623	94.0	40.0	35.0	
	673	99.0	36.0	45.0	

electrons/holes from the surface of the catalyst to the substrate molecule and is reversible,³² *i.e.* the greater the activation energy, the greater will be the energy required for electronic transitions resulting in decreased activity of catalysts. Further, it is observed that at 623 K the decomposition of benzyl alcohol on ZnMnFeO₄ ($\Delta E = 56.69$ kJ mol⁻¹) is



Fig. 3 (a) Effect of A-site ion concentration at 623 K and (b) saturation magnetization at 473 K on % decomposition of benzyl alcohol. (c) Effect of charge carrier on (\bigcirc), % dehydrogenation and (\bigcirc), dehydration selectivities at 623 K for the system $Zn_{1-x}Cu_xMnFeO_4$. Flow rate 0.092 cm³ min⁻¹

only 65% while at the same temperature CuMnFeO₄ ($\Delta E = 13.01 \text{ kJ mol}^{-1}$) gives 94% conversion [Fig. 1(d)].

Fig. 3(c) shows the effect of charge carriers on the dehydrogenation and dehydration selectivities. It can be seen that the dehydrogenation selectivity (benzaldehyde) decreases with the decreasing values of the Seebeck coefficient (Table 3). It is well known that p-type semiconductors are active and selective towards dehydrogenation owing to rapid migration of holes while dehydration is selectively favoured by n-type semiconductors owing to migration of electrons.³³ With substitution of Cu^{II} in the spinel lattice, the concentration of holes decreases as indicated by the thermoelectric power measurements (Table 3). Hence, dehydrogenation selectivity decreases from ZnMnFeO₄ to CuMnFeO₄. Similar observations have also been reported by Chakrabarty *et al.*¹ in the investigation of propan-2-ol decomposition over perovskite catalysts.

From Table 5, it is observed that incorporation of copper(II) in the lattice of ZnMnFeO₄, results in the decrease in the M—O stretching vibrations, indicating strengthening of metal-oxygen bonds so that lattice oxygen cannot be easily exchanged with the substrate molecule, resulting in decreased dehydrogenation activity. Thus at 473 K, ZnMnFeO₄ shows 91% dehydrogenation while at the same temperature CuMnFeO₄ yields only 54% dehydrogenation selectivity (Table 6).

The parallelism between the magnetic and catalytic properties of a compound is explained by Panchenkov and Lehdev.³⁴ The compound ZnMnFeO₄ is antiferromagnetic and the compounds with x = 0.2-0.4 do not saturate even at 77 K. The compounds with $0.6 \le x \le 1.0$ saturate at both 77 and 298 K. With increasing saturation magnetization [Table 4, Fig. 3(b)], catalytic activity shows an increasing trend, *i.e.*

Table 7 Conversion obtained after 60 min process time (T = 623 K, flow rate 0.092 cm⁻³ min⁻¹)

x	benzyl alcohol conversion (%)
0.0	54.0
0.2	63.0
0.4	68.0
0.6	72.0
0.8	80.0
1.0	90.6

with increase in the value of σ_s , the conversion of benzyl alcohol increases from 38 to 61%. This is due to increasing magnetic ordering (resulting from exchange interaction between Fe³⁺ ions present at A-sites), which facilitates the charge-transfer phenomenon involved in the absorption of alcohols. Similar results have also be reported by Narsimhan and Swamy³⁵ in the investigation of decomposition of propan-2-ol over the MgAl_{2-x}Fe_xO₄ system.

The oxidative dehydrogenation of benzyl alcohol has been studied with varying LHSV (3.18, 5.25, 12.36). It was observed that with increasing LHSV, % decomposition decreases but at the same time the benzaldehyde selectivity improves. It is due to the fact that increasing LHSV decreases the contact time of substrate with the catalyst.

Stability of the Catalysts Studied

Stability tests for each catalyst of the system $Zn_{1-x}Cu_xMnFeO_4$ were carried out. The ferrites showed good stability under highly reducing conditions. Two checks were made to determine the stability; (i) Conversion levels over a long period (process time 60 min after reaching a steady state) and (ii) comparison of X-ray diffraction lines of the used catalyst with those of the fresh one.

Conversion levels were steady and did not drop over 60 min after steady state was achieved. This enabled the evaluation of sustained activities of the catalysts in terms of conversion over 60 min process time (Table 7).

X-Ray diffraction patterns of the used catalysts did not show any additional lines, although there was slight decrease in the intensities as compared with fresh catalysts. Thus, there is no bulk reduction of the catalysts and the spinel structure is essentially retained under the reduced conditions. However, surface reduction could take place, which is not detectable by X-ray analysis. Further IR spectra of used catalysts did not show any change in the band positions. This is in contrast to Fe_2O_3 catalyst, which undergoes bulk reduction under reducing conditions.³⁵

Conclusions

On the basis of structural, transport, magnetic and Mössbauer studies; (1) The probable cation distribution of the system $Zn_{1-x}Cu_xMnFeO_4$ is suggested as:

$$Zn_{1-x}^{2+}Fe_x^{3+}[Fe_{1-x}^{3+}Cu_x^{2+}Mn_{1-y}^{3+}Mn_y^{4+}]O_4^{2+}$$

where y = 0.2. With the subsequent replacement of Zn^{2+} by Cu^{2+} in the system, an equal amount of Fe^{3+} migrates from octahedral to tetrahedral sites. (2) All the compounds exhibited p-type behaviour. (3) The compound $ZnMnFeO_4$ is antiferromagnetic while $CuMnFeO_4$ shows ferrimagnetic

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