X-ray, transport, magnetic and catalytic studies of the system $Cd_{1-x}Cu_xFeCrO_4$

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The compounds of the system $Cd_{1-x}Cu_xFeCrO_4$, where $0.0 \leqslant x \leqslant 1.0$, synthesized by the co-precipitation technique have been studied with a view to investigating the cation distribution and the transport and magnetic properties, and to correlating the physical properties of oxidic spinels with their catalytic behaviour in the decomposition of benzyl alcohol. All the compounds of the system were crystallized with the cubic-spinel structure. The activation-energy values of electronic conduction varied between 0.69 and 0.16 eV. Thermoelectric power measurements indicated a p-type semiconducting nature for all the compounds. Magnetic hysteresis studies indicated that the compounds with $x \geqslant 0.4$ were ferrimagnetic. The Curie temperatures increased with increases in the Cu^{2+}-ion concentration. A good correlation could be established between the physical properties and the catalytic behaviour of the system.

1. Introduction

Ternary oxides crystallizing with spinel structure have been found to exhibit interesting solid-state [1, 2] and catalytic properties [3, 4]. Spinel oxides are a class of ternary oxides with compositions AB_2O_4, where the A ions occupy a tetrahedral site and the B ions occupy octahedral sites. The properties of these compounds are controlled by the nature of the ions, their charges and their distribution amongst tetrahedral and octahedral sites. These oxides have been used as catalysts for various processes, such as the oxidation of hydrocarbons [3], and dehydration and dehydrogenation of alcohols [5, 6].

We studied the system $CdFeCrO_4–CuFeCrO_4$ with a view to investigating the effect of substitution of Cu^{2+} for Cd^{2+} ions, on the structural, transport and magnetic properties of the system and correlating them with the catalytic behaviour in benzyl-alcohol decomposition.

2. Experimental procedure

The various compositions of the system $Cd_{1-x}Cu_xFeCrO_4$, where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0, were prepared by the co-precipitation technique [7, 8]. Initially, specific amounts of the respective sulphates (BDH/AR) were dissolved in distilled water and hydroxide precipitation was carried out at a controlled pH of 9.0–9.5, using a standard sodium-hydroxide solution. The precipitate was heated in a water bath (90 °C) for 3–4 h and it was oxidized by adding the required (calculated) amount of 30% (100 vol.) H_2O_2 with constant stirring. The precipitate was filtered, washed and dried at 80 °C in a vaccum

cryostat. The compositions of the products were checked by chemical analysis and they were found to be within 1 % of the nominated values.

X-ray powder diffraction patterns were recorded on a diffractometer (Siemens D-500, Kristalloflex) with a microprocessor controller, using CuK_α radiation ($\lambda = 0.1540$ nm) with a Ni-filter. X-ray patterns of all the compositions indicated the formation of a single spinel phase. To measure the intensity, the areas under different $(h\,k\,l)$ peaks were determined and compared with the values obtained in relation to the peak area for the $(3\,1\,1)$ reflections which was taken as representing 100 per cent. To calculate the relative integrated intensity, I, of a given $(h\,k\,l)$ reflection, the following Buerger [9] formula was used, where the variables have their usual meaning

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

The atomic scattering powers for various ions were taken from the literature [10].

In order to determine the cation distribution and its variation with composition, the intensity ratios I_{440}/I_{422}, I_{220}/I_{440} and I_{422}/I_{400} were calculated for different possible models of cation distribution, as the reflections $(2\,2\,0)$, $(4\,0\,0)$, $(4\,2\,2)$ and $(4\,4\,0)$ are sensitive to cation distribution at both sites. These were then compared with the observed intensity ratios. The maximum standard deviation in the observed ratios was ± 0.02.

To measure electrical conductivity and thermoelectric power, pellets were prepared using 2 % polyvinyl acetate solution as a binder. The pellets were

TABLE I Lattice constant, a, activation energy, ΔE, thermoelectric coefficient, α, Curie temperature, T_c, and cation distribution for the system $Cd_{1-x}Cu_xFeCrO_4$

Composition x	Lattice constant a (nm)	Activation energy ΔE (eV)	Thermoelectric coefficient α ($\mu V\,K^{-1}$)	Curie temperature T_c (K)	Cation distribution[a]
0.0	0.861	0.69	+ 264	–	$(Cd^{2+})[Fe^{3+}Cr^{3+}]O_4$
0.2	0.853	0.61	+ 204	–	$(Fe^{3+}_{0.2}Cd^{2+}_{0.8})[Cu^{2+}_{0.2}Fe^{3+}_{0.8}Cr^{3+}]O_4$
0.4	0.851	0.54	+ 147	241	$(Fe^{3+}_{0.4}Cd^{2+}_{0.6})[Cu^{2+}_{0.4}Fe^{3+}_{0.6}Cr^{3+}]O_4$
0.6	0.844	0.46	+ 99.5	275	$(Fe^{3+}_{0.6}Cd^{2+}_{0.4})[Cu^{2+}_{0.6}Fe^{3+}_{0.4}Cr^{3+}]O_4$
0.8	0.839	0.27	+ 89.5	355	$(Fe^{3+}_{0.7}Cd^{2+}_{0.2}Cu^{2+}_{0.1})[Cu^{2+}_{0.7}Fe^{3+}_{0.3}Cr^{3+}]O_4$
1.0	0.830	0.16	+ 40.6	417	$(Fe^{3+}_{0.75}Cd^{2+}_{0.25})[Cu^{2+}_{0.75}Fe^{3+}_{0.25}Cr^{3+}]O_4$

[a]( )denotes a tetrahedral and [ ] an octahedral structure.

heated slowly in air to remove the binder and then sintered at 1173 K for 70 h.

Direct-current (d.c.) electrical-resistivity and thermoelectric-power measurements were carried out using an *LCR* Marconi bridge. The end faces of each pellet were coated with a thin layer of conducting silver paste and measurements were carried out from room temperature to 673 K, using the two-probe technique. Thermoelectric-coefficient measurements were performed from room temperature to 573 K.

The magnetic hysteresis loops at room temperature (300 K) and at liquid-nitrogen temperature (80 K) for all the compositions were taken, using an alternating-current (a.c.) electromagnet-type loop tracer [11]. The saturation magnetization, σ_s, at 300 K and 80 K was also recorded on a digital multimeter.

Initial susceptibility studies were carried out using the double coil method from room temperature to 470 K for the compounds with $x \geqslant 0.4$, with a field of 40 A m^{-1} [12]. From the plots of x/x_i against T, the Curie temperatures, (T_c) of the compounds were determined.

All the compositions of the system were then investigated for their catalytic activity towards decomposition of benzyl alcohol, in the temperature range 473–673 K, using a fixed bed, constant-flow reactor, made from a quartz glass. The 25 cm long (15 mm internal-diameter) reactor was fitted with a Chromel–Alumel thermocouple, to record the temperature of the catalyst bed, within a temperature range of ± 1 K.

3. Results and discussion

The results of X-ray analysis are given in Table I. It can be seen that all the compositions of the system possess cubic symmetry. The lattice constant decreases linearly (Fig. 1a) from $CdFeCrO_4$ ($a = 0.861$ nm) to $CuFeCrO_4$ ($a = 0.830$ nm), obeying Vegard's law [13]. The lattice-constant value obtained for $CuFeCrO_4$ was in good agreement with a value reported earlier [14]. The decrease in the lattice constant, as the value of x increases, is due to replacement of the larger Cd^{2+} ion (0.097 nm) by a comparatively smaller Cu^{2+} ion (0.072 nm) in the tetrahedral site [15]. The cation distributions at the two sites in the system were obtained by X-ray intensity calculations. The observed and calculated intensity ratios for the
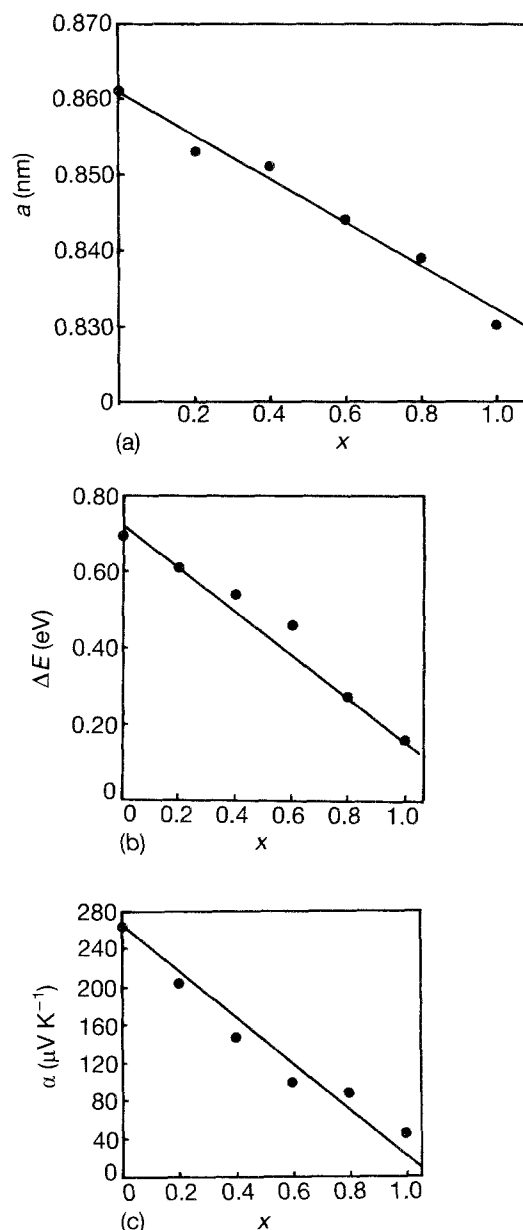

Figure 1 Plots of (a) the lattice constant, a, (b) the activation energy, ΔE, and (c) the thermoelectric coefficient, α, versus x for the system $Cd_{1-x}Cu_xFeCrO_4$.

compound $CuFeCrO_4$ using different models are summarized in Table II. From Table II it can be seen that the model in which both Fe^{3+} and Cu^{2+} ions are distributed between tetrahedral and octahedral sites

TABLE II A comparison of the intensity ratios of $CuFeCrO_4$

Cations		I_{440}/I_{422}		I_{220}/I_{440}		I_{422}/I_{400}	
A-site	B-site	Observed	Calculated	Observed	Calculated	Observed	Calculated
Fe^{3+}	$Cu^{2+}Cr^{3+}$		4.6224		0.5683		0.4564
$Fe^{3+}_{0.8}Cu^{2+}_{0.2}$	$Fe^{3+}_{0.2}Cu^{2+}_{0.8}Cr^{3+}$		4.2982		0.6093		0.5263
$Fe^{3+}_{0.75}Cu^{2+}_{0.25}$	$Fe^{3+}_{0.25}Cu^{2+}_{0.75}Cr^{3+}$	4.1886	4.2225	0.6135	0.6198	0.5386	0.5453
$Fe^{3+}_{0.6}Cu^{2+}_{0.4}$	$Fe^{3+}_{0.4}Cu^{2+}_{0.6}Cr^{3+}$		4.0069		0.6518		0.6068
$Fe^{3+}_{0.5}Cu^{2+}_{0.5}$	$Fe^{3+}_{0.5}Cu^{2+}_{0.5}Cr^{3+}$		3.8722		0.6735		0.6517
$Fe^{3+}_{0.4}Cu^{2+}_{0.6}$	$Fe^{3+}_{0.6}Cu^{2+}_{0.4}Cr^{3+}$		3.7442		0.6956		0.7000
$Fe^{3+}_{0.2}Cu^{2+}_{0.8}$	$Fe^{3+}_{0.8}Cu^{2+}_{0.2}Cr^{3+}$		3.5066		0.7409		0.8080
Cu^{2+}	$Fe^{3+}Cr^{3+}$		3.2909		0.7877		0.9337

shows better agreement. Details of the cation distribution of the ions in the system are given in Table I.

The room-temperature (RT) resistivity values, ρ_{RT}, of all the compounds of the system were found to vary between 10^7 and 10^3 Ω cm, for different values of x. The plots of log ρ versus $10^3/T$ showed a linear nature, obeying Wilson's law, $\rho = \rho_0 \exp(\Delta E/kT)$, indicating the semiconducting nature of all the compounds under investigation. The activation energy calculated from the slope of above plots for different compositions varied between 0.69 and 0.16 eV (Table I) with an increasing value of x, and this is plotted in Fig. 1b.

The thermoelectric-coefficient values, α, varied between $+264$ and $+40.6$ $\mu V\,K^{-1}$ (Table I) indicating that all the compositions were p-type charge carriers. The p-type behaviour decreases with increases in the value of x (Fig. 1c).

Magnetic hysteresis studies indicated that $CdFeCrO_4$ and $Cd_{0.8}Cu_{0.2}FeCrO_4$ are antiferromagnetic, while the remaining compounds tend to become increasingly ferromagnetic with an increase in Cu^{2+} ion concentration in the lattice. The Curie temperatures, T_C values of the compound were determined from x/x_i versus T curves. The T_C values of compounds ($x \geqslant 0.4$) increased with increasing Cu^{2+}-ion concentration, probably due to strengthening of the A–B interactions.
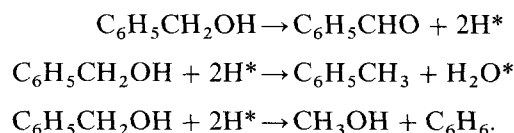
4. Catalytic studies

Each composition of the system was studied for its catalytic behaviour, using a 3 g powdered sample of the spinel. Benzyl alcohol was passed at a flow rate of

TABLE III Catalytic performance data for the decomposition of benzyl alcohol

Catalyst	Catalyst bed temperature	Conversion (%)	Selectivity (%)		
			Aldehyde	Toluene	Benzene
$CdFeCrO_4$					
	200	4.13	75.38	21.89	2.01
	300	13.01	73.53	23.19	2.17
	350	20.13	65.72	30.18	3.97
	400	28.19	57.31	36.89	4.19
$Cd_{0.8}Cu_{0.2}FeCrO_4$					
	200	6.09	73.17	24.62	1.98
	300	17.01	70.39	26.17	3.07
	350	25.11	63.51	32.19	3.79
	400	32.31	54.81	39.17	4.61
$Cd_{0.6}Cu_{0.4}FeCrO_4$					
	200	9.01	69.77	27.12	2.03
	300	19.13	65.93	31.01	2.61
	350	29.03	59.13	36.13	3.17
	400	39.17	51.13	43.07	4.69
$Cd_{0.4}Cu_{0.6}FeCrO_4$					
	200	11.11	67.01	30.12	1.56
	300	25.17	61.59	35.01	2.31
	350	33.29	55.93	40.13	3.63
	400	49.71	48.54	46.10	5.01
$Cd_{0.2}Cu_{0.8}FeCrO_4$					
	200	17.31	65.17	32.03	2.14
	300	31.39	59.30	36.90	3.29
	350	40.19	52.18	42.29	5.50
	400	59.71	46.13	48.23	7.30
$CuFeCrO_4$					
	200	22.61	64.23	33.13	2.63
	300	37.01	55.49	42.17	3.86
	350	49.50	49.28	44.19	6.61
	400	70.31	42.93	49.17	8.10

0.04 mol h^{-1} at various temperatures, and the products were collected in an ice-chilled collector. They were analysed for toluene, a dehydration product, and benzaldehyde, a dehydrogenation product, using a gas chromatograph. Another product was benzene, but since the yield of this was small, it is neglected from our discussion. The various products formed as a result of catalytic decomposition can be represented as follows

$$C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H^*$$

$$C_6H_5CH_2OH + 2H^* \rightarrow C_6H_5CH_3 + H_2O^*$$

$$C_6H_5CH_2OH + 2H^* \rightarrow CH_3OH + C_6H_6.$$

The decomposition of benzyl alcohol over different compositions of the system $Cd_{1-x}Cu_xFeCrO_4$ is summarized in Table III. Table III shows that copper-rich compounds are always more active than cadmium-rich compounds (Fig. 2). The increase in the benzyl-alcohol decomposition (%) with increasing concentration of Cu^{2+} ions in the lattice may be attributed to the fact that in the case of $CdFeCrO_4$ (normal spinel) the A-site is occupied by stable Cd^{2+} ions and the catalytic activity is mainly due to the hopping of B-site ions, while in $CuFeCrO_4$ (random spinel), the A-site is occupied by both Fe^{3+} and Cu^{2+} ions, which can change between the $+2/ +3$ and the $+1/ +2$ states, respectively, thus providing a greater number of adsorption sites for alcohol molecules to react. Therefore, with the increasing value of x in the spinel lattice the catalytic activity increases, indicating that cation distribution plays an important role in the decomposition of benzyl alcohol. Similar observations have also been reported by Cota et al. [16] and Onuchuwu [17] during investigations of hydrogen-peroxide decomposition over Ni-ferrite and Cu–Ni–ferrite catalysts, respectively.
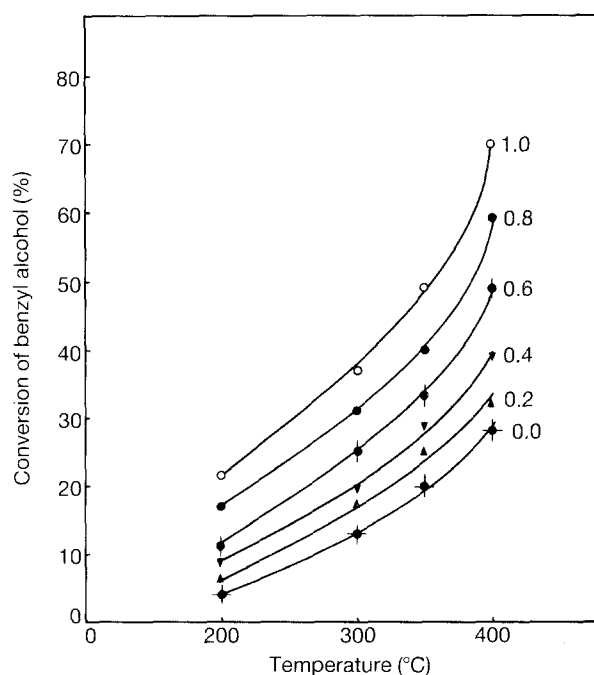
The effect of activation energy on the catalytic activity of various compositions of the system can also be seen in Table III, where it is observed that with a decrease in the activation energy, the decomposition of benzyl alcohol increases. This is due to the fact that catalysis involves transfer of electrons/holes from the surface of the catalyst to the substrate molecule and is reversible [6], i.e. the greater the activation energy, the greater will be the energy required for electronic transitions, resulting in a decreased activity of the catalysts. Further, it is observed that at 673 K the decomposition of benzyl alcohol on $CdFeCrO_4$ ($\Delta E = 0.69$ eV) is 28.19 %, while at the same temperature $CuFeCrO_4$ ($\Delta E = 0.16$ eV) gave a 70.31 % conversion.

The effect of charge carriers on the selectivities of dehydrogenation (benzaldehyde) and dehydration (toluene) can also be seen from Table III, where it is observed that the dehydrogenation selectivity decreases with decreasing values of the Seebeck coefficient. It is well known that p-type semiconductors are active and selective towards dehydrogenation due to rapid migration of holes, while dehydration is selectively favoured by n-type semiconductors due to migration of electrons [18]. With substitution of Cu^{2+} ions in the spinal lattice, the concentration of holes decreases, as indicated by the decreasing thermoelectric power measurements (Table I). Hence, dehydrogenation selectivity decreases from $CdFeCrO_4$ to $CuFeCrO_4$ (Fig. 3). Similar observations have also been reported by Chakrabarty et al. [19] in the investigation of propan-2-ol decomposition over perovskite catalysts.
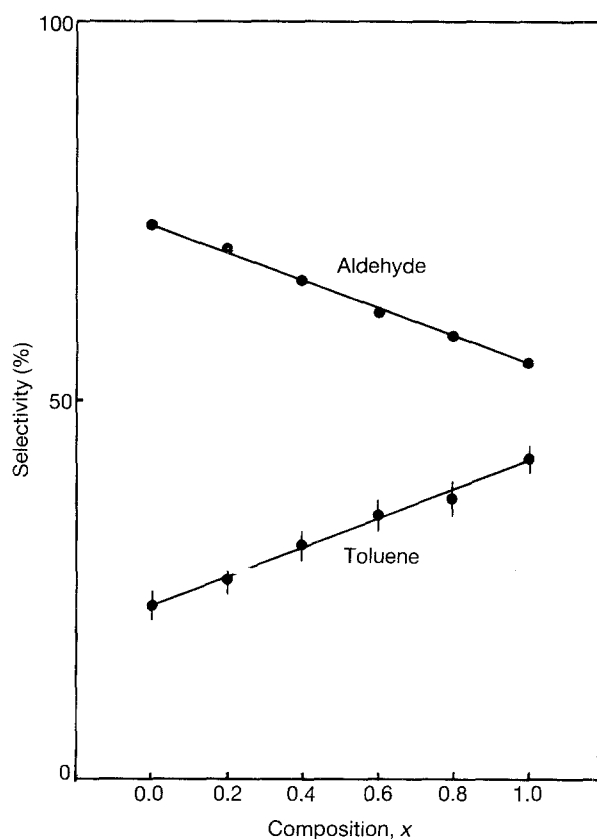

Figure 2 Conversion (%) of benzyl alcohol versus Temperature for the system $Cd_{1-x}Cu_xFeCrO_4$ for the x-values shown.

Figure 3 The effect of the composition, x, of the system $Cd_{1-x}Cu_xFeCrO_4$ on aldehyde and toluene selectivity at 300 °C.

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