

Catalytic Activity of Semiconducting CuO-Fe₂O₃ as Spinel Nanoferrite on the Thermogravimetric Studies on Lanthanum Oxalate Decahydrate

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ABSTRACT: Lanthanum Oxalate decahydrate and Copper ferrites were prepared by chemical and sintering process respectively and the detailed investigation of their properties was carried out successfully at room temperature by FTIR, XRD, SEM, TEM as well as by chemical methods. Catalytic activity of copper ferrite over the decomposition of lanthanum oxalate was studied non isothermally by TG-DTA after mixing the former with the later in varying mole ratios. Also a physical mixture of CuO and Fe₂O₃ was prepared for comparative study. It is found that CuO has catalytic activity whereas Fe₂O₃ behaves as negative catalyst for the entire process. But the physical mixture enhances the rate of reaction at the low temperature and as the temperature becomes high the solid solution of copper ferrite is expected to be formed by valence induction generating n- type semi conduction in Fe₂O₃ resulting in a ferrite having inverse spinel structure and having high rate constant. There is no appreciable change in activation energy during the process. It is inferred that the catalytic activity appears to be a function of semiconducting property of the copper ferrite. The formation of ferrite at high temperature is diffusion controlled best fitting third order law decomposition of Lanthanum Oxalate. The mechanism of decomposition has been proposed.

Keywords: Copper ferrite, Catalytic activity, Thermogravimetry, Inverse spinel, Valence induction

1. INTRODUCTION

Mechanical addition of Foreign Substances with metal salts results significant changes in thermo chemical behavior of materials which may arise due to catalytic activation of the additives [1] and sometimes the later may react with reactants resulting in the formation of new substances. The role of oxide additives especially the transition metal oxides on the decomposition of oxy salts now a day is an emerging field of research which catalyze the decomposition by favoring electron transfer process or decelerated by the Cage effect[2]. In recent years, many efforts have been directed towards the design of catalytic materials based on transition-metal mixed oxides as a replacement for noble metal catalysts. Among them, ferrites widely have been used as active catalysts in various catalytic reactions, as hydrocarbon oxidation, oxidative dehydrogenation, decomposition of alcohols and peroxides and decarboxylation of some organic acids, oxidation of carbon monoxide [3], electro-catalytic activity [4],[5],[6],[7]. The use of ferrites based catalysts M^{II}Fe^{III}₂O₄, (M = Cu, Co and Cr) are of great importance particularly for total oxidation of light hydrocarbons[8],[9]. The interaction between metallic cations results in the key factor for the catalytic process. Chemical composition, crystal structure, electronic, electrochemical, and micro structural factors have been found to contribute to the overall activity of such catalysts [10]. Copper is one of the most used metals in several catalytic reactions. The distribution of Cu in the two different crystal sites in this structure keep the active sites separated, prolonging the activity and stability of catalysts [11]. In the spinel ferrites MFe₂O₄, the metallic cations M²⁺ and Fe³⁺ can occupy octahedral and tetrahedral sites. If the M²⁺ cations occupy tetrahedral sub lattices in the cubic closed- packed O²⁻ lattice, the spinel ferrite is a normal spinel, otherwise, the ferrite is an inverse spinel. If both of the sub lattices contain M²⁺ and Fe³⁺ cations, the ferrite is a mixed spinel. The occupations of cations at these sites have an important effect on the properties of spinels, such

as magnetic behavior, conductivity and catalytic activity [12],[13],[14]. Copper ferrite in the analogous way is found to have remarkable activity simultaneously decreasing the reaction temperature[16]. The catalytic performance of nano CuFe₂O₄ on the thermal decomposition of ammonium perchlorate show that the later has high a catalytic activity, and the decomposition temperature of ammonium perchlorate shift 105 °C downward with the effect of catalyst. When the content of CuFe₂O₄ comes to 5%, the catalytic performance is the best.[17]. Since semiconducting oxides CuO alone behaves as a good catalyst increasing the decomposition manifold[18], a series of single and mixed oxides of CuO- Fe₂O₃ was prepared and the catalytic activity of the obtained pure and mixed oxides was measured using the decomposition of hydrogen peroxide at 30–50°C. It was found that the mixed oxide solids have catalytic activity higher than single oxides preheated at 350 °C and 550°C. The rise in precalcination temperature to 750°C and 1000°C brought about a drastic decrease in the activity of mixed solids because of formation of copper ferrite phase and/or sintering process [19]. The catalytic activity of Copper iron composite oxide on CO oxidation were evaluated by using a micro reactor-GC system indicated obviously high stability and catalytic activity on CO oxidation at low temperature. The effect of the calcination temperature, the molar ratios of copper to iron, the specific surface areas and the particle sizes on the catalytic activity of the catalysts was investigated[20]. In this paper, we present a study on copper ferrite prepared by nonconventional methods and effect of their chemical composition and the calcinations temperature on the mutual solid–solid interaction and physicochemical properties of CuO-Fe₂O₃ system, as catalyst for lanthanum oxalate oxidation. The catalytic activity of the pure and mixed oxide catalysts produced at temperature ranged between 350 °C and 750°C was measured in lanthanum oxalate decomposition reaction. Catalytic effect of Magnesium chromites has already been studied and it has been found

that the activity is concentration and temperature dependent[15].

2. MATERIALS AND METHODS

2.1.Preparation of lanthanum oxalate

La(III) Oxalates was prepared from $\text{La}(\text{NO}_3)_3$ by drop wise addition of a hot 4% ammonium oxalate solution to a stirred hot solution of $\text{La}(\text{NO}_3)_3$, after their dissolution in nitric acid. It was then neutralized to pH 7 with (1:1) NH_4OH . The precipitates formed were left to stand at room temperature for 1 h, filtered off, washed with a diluted ammonium oxalate solution and finally dried at 80°C to a constant weight.

2.2.Preparation of $\text{CuO-Fe}_2\text{O}_3$ mixed metal oxide/ CuFe_2O_4 catalyst

For preparation of $\text{Fe}_2\text{O}_3/\text{CuO}$ pellets, Fe_2O_3 and CuO powders were mixed in the de-ionized water in a stirring tank equipped for 30 minutes at room temperature. The well-mixed $\text{Fe}_2\text{O}_3/\text{CuO}$ slurry solution was dried at 80°C for 6 hours, and then pulverized $\text{Fe}_2\text{O}_3/\text{CuO}$ particles were sintered in a muffle furnace at 850°C for 24 hours. The powder is then characterized.

2.3.Preparation of mixture

A mixture of the prepared lanthanum oxalate was prepared with crystalline copper ferrite; $\text{Fe}_2\text{O}_3/\text{CuO}$ in three different mole percentage i.e. 2, 5 and 10 mol%, by thorough grinding in an agate mortar for uniform mixing with regular particle size. Then the mixture of uniform mesh size was subjected to thermal analysis.

3.RESULT AND DISCUSSIONS

3.1.FTIR ANALYSIS

The infrared spectra of the prepared solid catalysts were studied by FT-IR spectroscopy (**Jasco FT-IR 4100 spectrometer (Japan)**) employing samples prepared as KBr disks in the range 400 cm^{-1} to 4000 cm^{-1} (Fig 1). The characteristic absorption are obtained in the regions 3418, 3412, 1629, 1123, 1614, 548, 532, 456 and 450 cm^{-1} . The general range of $3600\text{--}3100\text{ cm}^{-1}$ is assigned to antisymmetrical and symmetrical O–H bonding stretching vibrational modes for water of hydration. The bonding in the region of $1670\text{--}1600\text{ cm}^{-1}$ also relates to O–H bonding bending vibrational modes. The bands at 455 and 548 cm^{-1} observed in the samples can be attributed to metal oxygen stretching vibrational modes. These show two strong bands at about 573 cm^{-1} and 432 cm^{-1} which confidently can be assigned to the stretching vibration of the bonds Fe(III)–O in tetrahedral and octahedral building units of inverted spinel, respectively. Furthermore, the most distinctive feature of the spectrum is that two new intense bands at 600 cm^{-1} and 400 cm^{-1} appear which are assigned to CuFe_2O_4 . These characteristic two band spectra, which belong to the pure spinel structure, are maintained in the solids calcined at 400°C and 700°C .

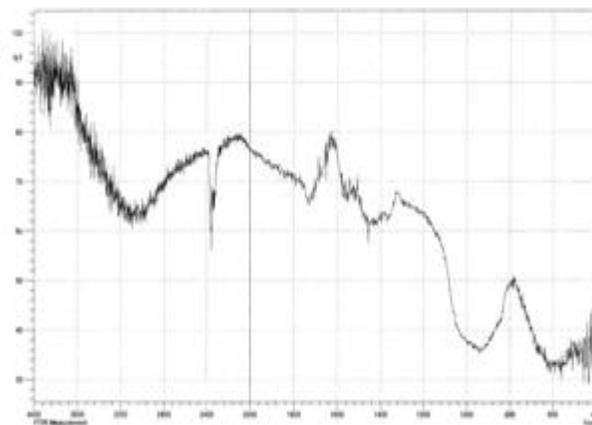


Fig. 1. FT-IR spectrum of CuFe_2O_4 catalyst.

3.2. XRD ANALYSIS

Copper iron composite oxide catalysts calcined at different temperature are examined by XRD (Table 1). The catalysts are amorphous when the calcination temperature is below 300°C , and the catalysts become more crystalline when the calcinations temperature increases from 400 to 600°C . The crystallinity of the catalysts became better with the increase of the calcinations temperature. Inspection of the above figures shows that, well crystalline phases of CuO (monoclinic) and $\alpha\text{-Fe}_2\text{O}_3$ (rhombohedral) were detected for all the mixtures thermally treated at 350°C (Fig 2). The disappearance of all the diffraction lines of CuO phase suggested its presence in small-sized crystallites that can be detected by XRD investigation. This behaviour expected to be accompanied by an increase in the degree of dispersion of CuO and consequent increase in its catalytic activity. The increasing of treatment temperature up to 550°C was followed by a significant increase in the intensities of the X-ray patterns of ferric oxide phase. The XRD diffractograms of the analyzed samples calcined at different temperatures are depicted in Fig.3. The refinements revealed the formation of tetragonal copper ferrite in both synthesis routes. Because the calcination temperature was 800°C , sample contains a significant amount of $\alpha\text{-Fe}_2\text{O}_3$ and CuO besides the copper spinel. After the catalytic tests, the phase distribution in the sample was changed; copper ferrite became cubic and $\alpha\text{-Fe}_2\text{O}_3$ is transformed into $\gamma\text{-Fe}_2\text{O}_3$. The changes induced by the catalytic tests are much more evident, as considerable amount of CuFe_2O_4 appears in the sample.

3.3.SEM AND TEM ANALYSIS

TEM measurements of the sample were carried out using a JEOL transmission electron microscope. Sample for the TEM was prepared by making a clear dispersion of nanoparticles in dimethyl formaldehyde and putting a drop of it on a carbon-coated copper grid. The general morphologies and microstructure of the catalysts calcined at different temperature were investigated by transmission electron microscopy (TEM) and shown in Fig.4 & Fig 5.

Table-1. X-Ray Diffraction patterns for the various samples

Samples	'd' values Å ⁰	JCPDS Values
CuO	2.519	2.523
	2.3234	2.323
	1.8643	1.866
	1.4104	1.410
Cr ₂ O ₃	3.6838	3.684
	2.695	2.700
	2.2039	2.207
	1.8397	1.8486
	1.694	1.6941
	1.4895	1.4859
	1.4528	1.4538
CuFe ₂ O ₄	1.599	1.5932
	2.5631	2.5817
	2.1422	2.158
	2.0475	2.0666
	1.4729	1.4611

The TEM images reveal that most of the nanoparticle catalysts are uniform in size (with a narrow distributing). From the average nanoparticle sizes obtained from the TEM images, it can be seen that the particle size increased with increasing the calcinations temperature from 300°C to 600°C, and it is noted that the particle sizes of the samples calcined at 200°C and 300°C are almost the same. SEM was done 'JEOL JSM-6610LV' Scanning Electron Microscope. For SEM analysis, the sample was dispersed on the aluminum stub used for sample mounting. The sample was scanned at an accelerating voltage of 20 kV at a working distance of 15mm. The particle size was measured at a magnification of 10kX (Fig 6).

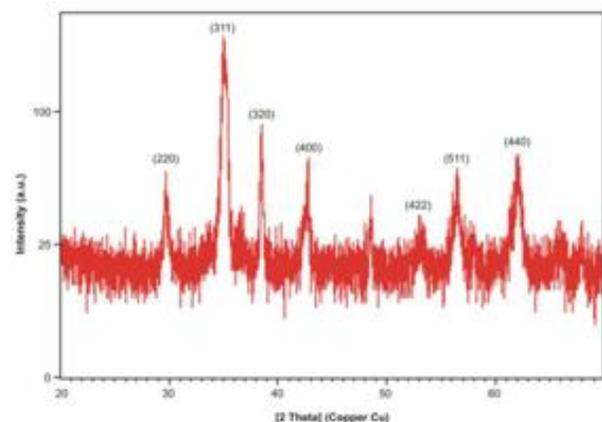


Fig. 2. XRD spectrum of native CuFe₂O₄ catalyst calcined at 350°C

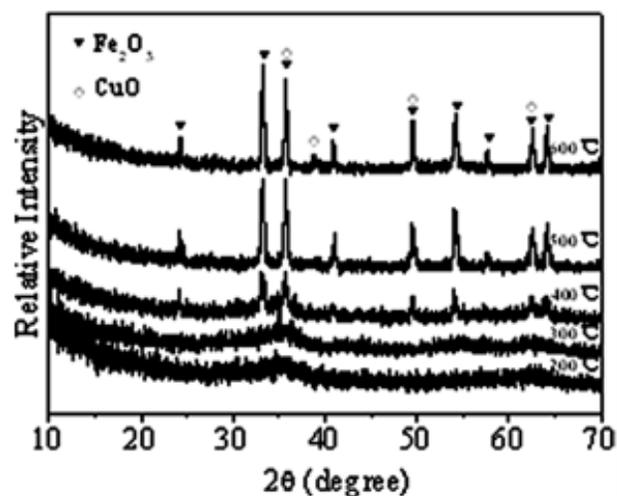


Fig.3 XRD patterns of the catalysts calcined at different temperatures

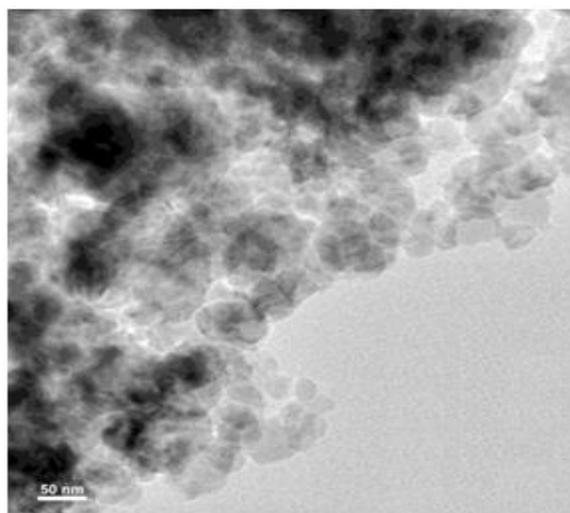


Fig. 4. TEM image of CuFe₂O₄ catalyst calcined at 350°C

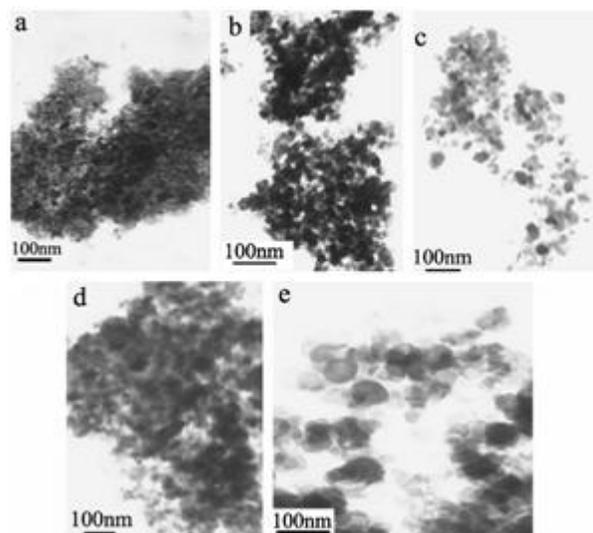


Fig.5 TEM images of the catalysts calcined at different temperature (a) 200°C, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C

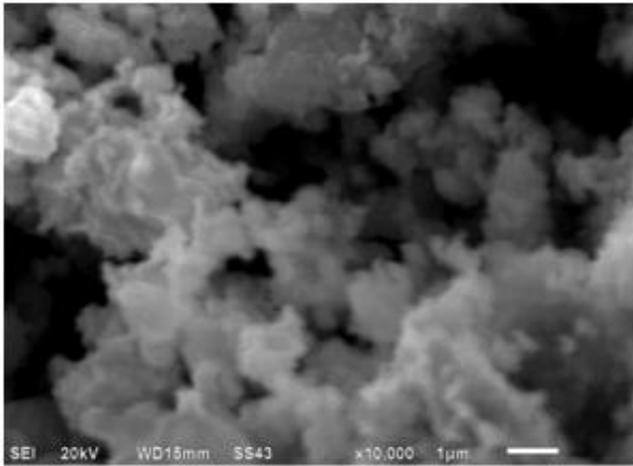


Fig. 6. SEM image of $CuFe_2O_4$ catalyst

3.4. THERMAL ANALYSIS

Thermogravimetric curves for lanthanum oxalate mixed with mixed transition metal oxide $CuO-Fe_2O_3$ shows significant increase in fractional decomposition α with respect to pure lanthanum oxalate although the decomposition temperature remain undisturbed i.e. at 653K (Fig.7, 8 &9). Mixture of lanthanum oxalate with simple oxides CuO, Fe_2O_3 , Physical mixture of $CuO-Fe_2O_3$ and mixed oxide of $CuO-Fe_2O_3$ sintered at $750^\circ C$ in three different mol% i.e. 2, 5, & 10 show two step decompositions, one acceleratory and decay stages. However mixture of lanthanum oxalate with Fe_2O_3 decomposes at comparatively higher temperature 663K, with lowest fractional decomposition α of all other categories of sample. Physical mixture of the the oxides CuO & Fe_2O_3 catalyses the decomposition there by remarkable change in fractional decomposition α . But at low temperature low concentration of catalyst (2 mol%) has increasing α values more than individual oxides as well as the mixed oxide ferrite for both the stages. Samples prepared with three different mole percentages of mixed metal oxide spinel ferrites show similar trends with no highest α values than the others but as the temperature gradually increases at moderate values 5 mol% has highest activity but after 723K the other three curves criss cross each other with 5mol% and 10 mol% show equal activities with highest fractional decomposition α even more than the physical mixture.(Fig.9)

3.5.KINETIC ANALYSIS:

The thermo gravimetric data are analysed and the fractional decomposition, α are plotted against temperature T(Fig .7) for different categories of samples. The plots are also drawn for the mixture with different concentration of the spinel type mixed oxides of copper and iron.(Fig.9). It is evident from the data that Fe_2O_3 being a negative catalyst retards the decomposition of lanthanum oxalate where as CuO significantly accelerate the decomposition. as far as the mixed $CuO-Fe_2O_3$ oxide is concerned the catalytic activities become even more with highest value of rate constant. The catalytic activity of mixed $CuO-Fe_2O_3$ obtained by thermal treatment of the $Cu-Fe$ mixtures at the same calcinations temperatures was found to be greater than that of single oxides (Table 2).

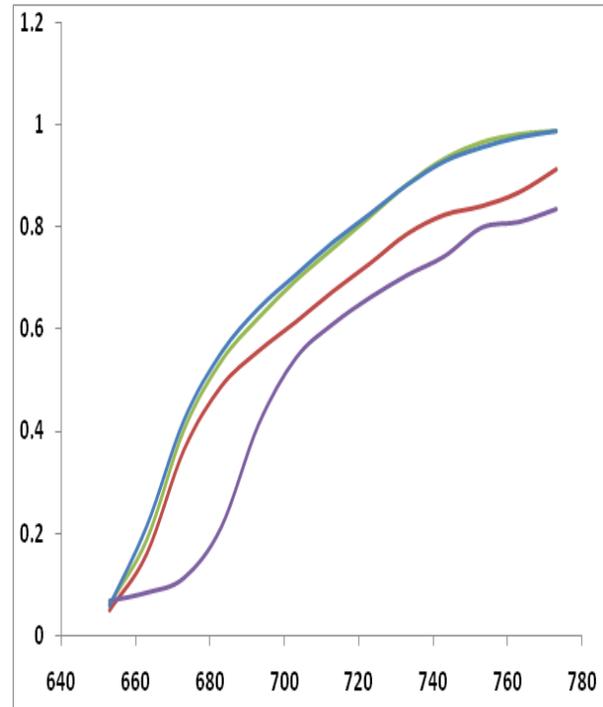


Fig.7 α -T curves for decomposition of pure lanthanum oxalate(red), and its mixtures with 5% Fe_2O_3 (violet), 5% CuO (Green),5% $CuO+Fe_2O_3$ (Blue)

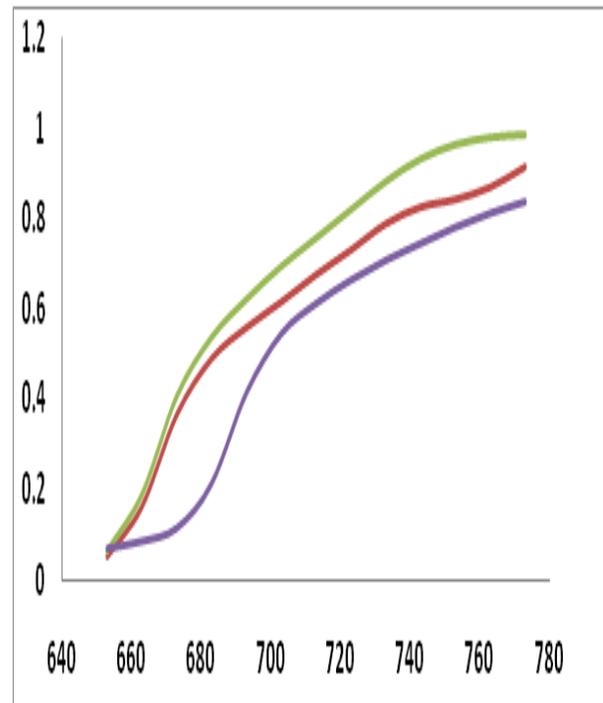


Fig.8. α -T curves for decomposition of lanthanum oxalate(red), mixed with5% Fe_2O_3 (violet), 5% CuO (Green)

The completion of reaction takes place in one step in case of pure lanthanum oxalate and its mixture with Cr_2O_3 , however for the other samples the reaction is two step i.e. one acceleratory and the other decay stage. But for comparative study all the data are analysed as one step

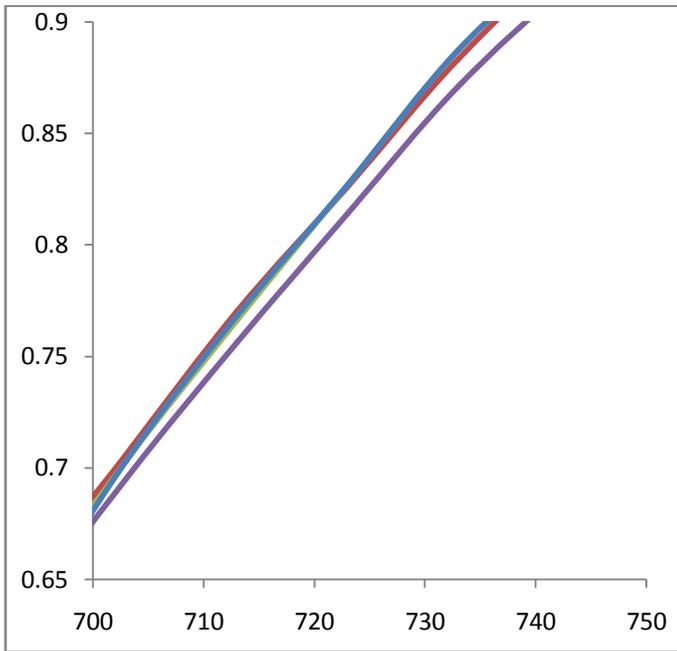


Fig.9. α -T curves for decomposition of lanthanum oxalate mixed with CuO+Fe₂O₃(violet), 2% CuFe₂O₄(blue), 5% CuFe₂O₄(Green), 10% CuFe₂O₄(red)

process. The kinetic parameters for the decomposition stage were determined using Coat-Redfern equation.

$$\log g(\alpha)/T^2 = \log(AR/\beta E) - E/2.0303RT \quad (1)$$

Where A is the pre exponential factor, β the heating rate, E the activation energy, R the universal gas constant and T the absolute temperature. $\log g(\alpha)/T^2$ is calculated for each possible rate controlling mechanisms using various solid state models and plotted against $1/T$ (Fig.10), using best fit model for the reaction. The value of $g(\alpha)$ with highest coefficient of linear regression analysis gives the idea about the best fit mechanism (Table 3) the best fit model F3 i.e the third order law is chosen for the entire temperature range 653-773K in order to compare all the data.

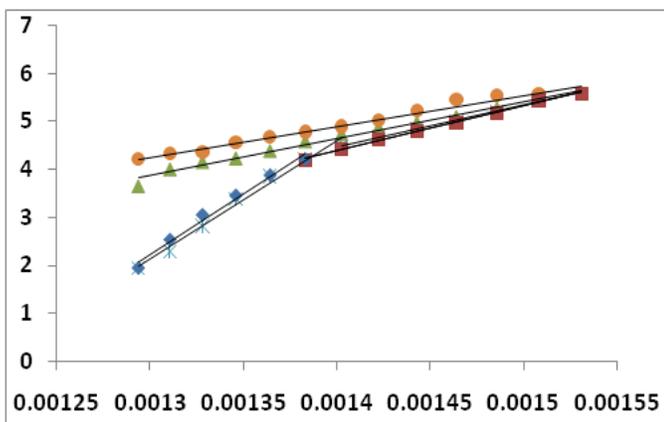


Fig.10. Variation of $-\log g(\alpha)/T^2$ against $1/T$ using F3 mechanism for the various samples depicted in Fig.9

The activation energy, E and pre-exponential factor A were calculated from the slope and intercept respectively of the Coat-Redfern equation and the plausible mechanism and the corresponding kinetic and thermodynamic parameters are listed in Table-3 using equations [15]

$$\Delta H^* = E - RT \quad (2)$$

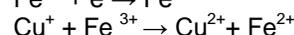
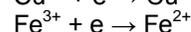
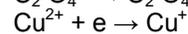
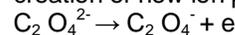
$$\Delta S^* = R[\ln(hA/k_B T) - 1] \quad (3)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (4)$$

ΔH^* , ΔS^* and ΔG^* are the enthalpy, entropy and free energy change of activation respectively. h the plank's constant and k_B the Boltzman's constant. The rate of the reaction was determined corresponding to the highest value of fraction decomposed i.e. α_{max} and the corresponding temperature T_s in the DTG plots (Fig.11(a) & (b)) whose value is 675K. It was found that the rate of the reaction is highest in case of mixture of sintered oxide of copper and iron (2 mol%) where copper ferrite is expected to be formed. However on increasing the concentration to 5 mol% the rate constant k decreases which again increases on increasing concentration to 10 mol%. Again it is found that the physical mixture of CuO and Fe₂O₃ shows more value for 'k' than the individual single oxides and even more than rate of decomposition of pure Lanthanum Oxalate.

4. ROLE PLAYED BY THE OXIDE

The above fact can be interpreted in terms of the concept of bivalent catalytic centres by assuming that for CuO the centres consist of Cu²⁺ - Cu⁺ ion pairs and for Fe₂O₃ they consist of Fe³⁺ - Fe²⁺ ion pairs. The observed increase in the catalytic activity of all CuO-Fe₂O₃ catalysts calcined at 400°C in comparison to pure Fe₂O₃ can be interpreted in terms of the concept of bivalent catalytic centres such as Cu²⁺-Fe³⁺ and/or Cu⁺-Fe²⁺ ion pairs beside the one component sites Cu²⁺-Cu⁺, Fe³⁺-Fe²⁺. The presence of Cu²⁺-Fe³⁺ and/or Cu⁺-Fe²⁺ ion pairs is a result of mutual charge interaction that is involved in La₂(C₂O₄)₃ decomposition reaction. From the electronic theory of catalysis and the principle of bivalent catalytic sites there are two kinds of catalytic sites in equilibrium on the catalyst surface, i.e. donor and acceptor sites, which may be formed by metal catalyst ions in various valence states or by charge defects stabilized on the catalyst surface. Therefore, the catalytic reactions proceed on the catalytic sites constituted from the ion pairs (Fe³⁺-Fe²⁺) and/or (Cu²⁺-Cu⁺) where one of the ions occurs in a lower and the second ion in a higher oxidation state. The higher catalytic activity of the two component oxides may be due to the fact that beside the one component sites Cu²⁺-Cu⁺, Fe³⁺-Fe²⁺, there will be also the mixed sites Cu²⁺-Fe⁺ and/or Cu⁺-Fe²⁺ ion pairs as a result of mutual charge interaction. In other words, the increasing activity of mixed oxides might be attributed to increase in the concentration of active sites via creation of new ion pairs.



In this case, the presence of reduced copper in the system is capable to reduce Fe³⁺ ion (major catalytic centres) partly

Table 2. Comparison of fractional decomposition for various samples

T, K	α' s					$-\log g(\alpha)/T^2$				
	Pure $\text{La}_2(\text{C}_2\text{O}_4)_3$	CuO	Fe_2O_3	$\text{CuO}+\text{Fe}_2\text{O}_3$	CuFe_2O_4	Pure	CuO	Fe_2O_3	$\text{CuO}+\text{Fe}_2\text{O}_3$	CuFe_2O_4
653	0.0492	0.061	0.068	0.057	0.061	5.586005	5.575158	5.568658	5.57885	5.575158
663	0.16	0.187	0.084	0.213	0.223	5.491586	5.463208	5.566818	5.434977	5.423869
673	0.364	0.403	0.113	0.421	0.4155	5.262944	5.207979	5.551877	5.181387	5.189599
683	0.488	0.537	0.212	0.553	0.541	5.087381	5.000003	5.461894	4.969456	4.992467
693	0.557	0.622	0.413	0.64	0.627	4.974274	4.83645	5.218743	4.794071	4.824884
703	0.614	0.695	0.543	0.706	0.695	4.867085	4.66251	5.013743	4.630605	4.66251
713	0.674	0.758	0.61	0.77	0.756	4.732614	4.47381	4.888308	4.429635	4.480959
723	0.729	0.821	0.662	0.826	0.814	4.584215	4.223983	4.77611	4.199375	4.257302
733	0.787	0.884	0.706	0.883	0.871	4.386967	3.859124	4.666903	3.86658	3.951387
743	0.824	0.934	0.743	0.929	0.916	4.233003	3.381065	4.561844	3.444494	3.590536
753	0.841	0.966	0.799	0.956	0.948	4.156384	2.816548	4.359982	3.040495	3.185597
763	0.868	0.982	0.81	0.976	0.97	4.006197	2.275594	4.322556	2.525472	2.719292
773	0.913	0.988	0.835	0.988	0.985	3.655397	1.934721	4.211327	1.934721	2.128542

Table-3. Arrhenius parameters for the decomposition of various samples using Coat-Redfern equation

Samples	$E(\pm 0.05), \text{KJmol}^{-1}$	$\log A(\pm 0.02), \text{s}^{-1}$	K^*, s^{-1}	$\Delta H^* \text{KJmol}^{-1}\text{K}^{-1}$	$\Delta S^* \text{KJmol}^{-1}$	$\Delta G^* \text{KJmol}^{-1}$
$\text{La}_2(\text{C}_2\text{O}_4)_3$ Pure	145.622	10.944	0.475	140.010	-50.513	-174.106
$\text{La}_2(\text{C}_2\text{O}_4)_3$ +CuO(5%)	286.922	22.181	0.9557	281.310	164.595	-170.208
$\text{La}_2(\text{C}_2\text{O}_4)_3$ + Cr_2O_3 (5%)	122.968	8.965	0.2823	117.356	-88.395	-177.023
$\text{La}_2(\text{C}_2\text{O}_4)_3$ +Physical Mixture of CuO and Cr_2O_3 (5%)	272.616	21.083	0.9766	267.004	143.585	-170.084
$\text{La}_2(\text{C}_2\text{O}_4)_3$ + CuFe_2O_4 (2%)	284.702	22.819	0.9786	279.090	176.818	-159.738
$\text{La}_2(\text{C}_2\text{O}_4)_3$ + CuFe_2O_4 (5%)	255.498	19.724	0.902	249.886	117.569	-170.527
$\text{La}_2(\text{C}_2\text{O}_4)_3$ + CuFe_2O_4 (10%)	270.843	20.941	0.9642	265.231	140.853	-170.155

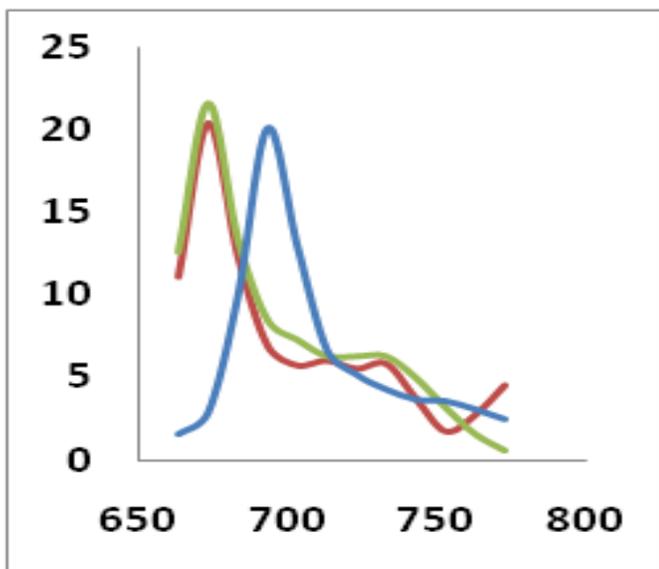


Fig.11(a) DTG plots of Pure $\text{La}_2(\text{C}_2\text{O}_4)_3$ (red) , $\text{La}_2(\text{C}_2\text{O}_4)_3$ + 5mol%CuO(green) and $\text{La}_2(\text{C}_2\text{O}_4)_3$ + 5mol%Cr₂O₃(blue)

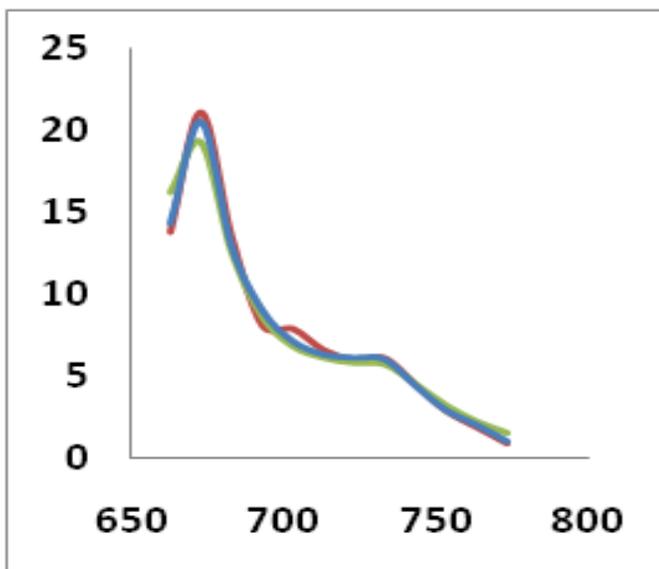


Fig.11 (b) DTG plots of Pure lanthanum oxalate with 2mol%CuFe₂O₄ (red), 5mol%(green) and 10mol% CuFe₂O₄(blue)

to ions of lower oxidation state (Fe^{2+}) minor centres being more active species in lanthanum oxalate decomposition. This means that the observed changes of the catalytic activity are probably due to the changes of the valence state of the catalytically active components of the catalyst. Increasing of calcinations temperature from 350°C to 550°C was accompanied by a progressive decrease in the catalytic activity of mixed solids. This because of increasing the degree of crystallinity of oxide phases which was accompanied by increasing their particle size and consequently decreasing the surface areas of the above phases leading decrease their catalytic activity. The constancy of the values of activation energy points to the similar nature of active centres being different from that of

single copper or ferric nitrates pre-calcined at the same temperatures. On increasing the calcination temperature of mixed solids to 750°C, no measurable catalytic activity showed because of the formation of the spinel form of copper ferrite (CuFe_2O_4). The poor performance of mixed solids precalcined at 750°C is explained in terms of the restricted redox couple represented by $\text{M}^n / \text{M}^{n-1}$ in the electronic composition of the catalysts and, possibly, the absence of M^n on the octahedral lattice site which may initiate the cyclic electron-transfer process on the catalyst surface. Alternatively, the modification of the surface area of the catalysts might be another critical reason for promoting the catalytic activity. Also, this behaviour was due to greater lattice oxygen mobility in the mixed oxide catalysts than single one. The presence of Cu decreases the strength of nearly Fe–O bonds, thus increasing the mobility of lattice oxygen and facilitating redox reactions on the catalyst surface.

5. CONCLUSION

The pre-calcination of mixed solids at 750°C showed the formation of well crystalline copper ferrite phase as a result of the solid–solid interaction between the corresponding oxides. The XRD intensities for the copper ferrite phase were affected by the calcination temperature. Mixed oxide solids obtained at 350°C and 550°C had catalytic activities higher than those of pure oxides obtained at the same temperature. There was no measurable catalytic activity for solids pre-calcined at 750°C because of the formation of inactive copper ferrite phase

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