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Photo catalytic studies of nano mixed metal oxides on Methyl Orange and Eriochrome Black-T

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ABSTRACT

The photo catalytic activity of nano mixed metal oxides $MCr_{1-x}Ba_xO_{3-\delta}$ were investigated by irradiating methyl orange and EBT with UV light.The $MCr_{1-x}Ba_xO_{3-\delta}$ (M=La and Ce) nano mixed metal oxides were synthesized by sol-gel method in different mole ratios (x=0,0.6 and 1). The structural phase, thermal behaviour, surface morphology and vibrational frequencies of catalysts were studied by XRD, TGA, SEM and FT-IR respectively. The efficiency of the catalystswere studied under UV-visible spectrometer. Amongdifferent mole ratios of $MCr_{1-x}Ba_xO_{3-\delta}$ (M=La and Ce), $CeCr_{0.4}Ba_{0.6}O_{3-\delta}$nano mixed metal oxide showed effective photo-degradation for EBT than methyl orange dye.

Keywords: Mixed Metal Oxides, Heterogeneous Catalysts, Photo Catalysis, Dyes

1. INTRODUCTION

The discharges of dyes from various industries are considered to be the serious cause for environmental pollution. Therefore, the released effluents have to be degraded before it enters the water bodies[1].The principle of photocatalytic reaction was to accelerate photoreactions in the presence of mixed metal oxide catalyst using light as energy[2].Nano structured mixed metal oxides have find vital applications in heterogeneous photocatalysis due to their multidisciplinary area of research[1-3].The irradiation of UV light on a semiconductor surface is an advanced oxidation process through heterogeneous photocatalysis[3].The use ofeco-friendly precursors, low reaction temperatures, and secondarypollution are the important issues meriting key consideration in dye degradation[4].Inorder to overcome the environmental problems, the doping of transition metals in metal oxides plays a very important role in photocatalytic studies[5].

Over the years rare earth transitionmetaloxides display a wide role in physics, chemistry and material science [6]. The advantages of using mixed metal oxide catalyst are its heat resistivity resistance to chemical attack, thermal stability, mechanical strength and so on[7, 8].Thetechnological applications of nano mixed metal oxides includephosphors, sensors, fuel cells, and as catalysts [9-18].

The present work aims to synthesize La and Ce containing mixed metal oxides by sol-gel method and the synthesized mixed metal oxides were characterized by various analytical techniques like FT- IR, SEM, TG and

XRD to determine their vibrational frequencies, surface morphology, thermal behavior and chemical composition of the oxides respectively. This study also presents the photo catalytic potential of mixed metal oxides using methyl orange and EBT as dyes.

II REVIEW OF THE LITERATURE

K.N Harish et al synthesized solar light active $CdFe_2O_4$ photocatalystby sol-gel auto combustion method and evaluated the photo-catalytic activity of the same by the degradation of methylene blue. The results revealed that $CdFe_2O_4$has effectively degraded the pollutant in waste water and hence it acts as a recyclable photocatalyst under solar light [19].Shivaraju.H.P studied the photocatalytic degradation of organic pollutants in the municipal sewage water by using TiO_2 deposited calcium alumino silicate beads, prepared by hydrothermal technique. The experimental parameters such ascatalyst load, pH, organic concentration, irradiation time, aeration, stirring, and light sources were investigated. The results indicated higher degradation efficiency, easy recovery and reuse of the photocatalyst [20].Ming Yang et al analyzed the evolution of hydrogen in the presence of UV-light irradiation using $Na_{1-x}La_xTa_{1-x}Cr_xO_3$ and $NaTa_{1-x}Cr_xO_3$mixed metal oxides.The photocatalytic activities was found to be much higher in $Na_{1-x}La_xTa_{1-x}Cr_xO_3$ than $NaTa_{1-x}Cr_xO_3$due to lesser Cr^{+6}, which is induced by co doping of lanthanum and chromium.

Photocatalytic degradation of phenolic compounds and other organic pollutants present in effluent of dye industry was evaluated by Raquel Cruz et al [21] using TiO_2 Degussa P-25 as photocatalyst. The solutions were illuminated under lamp at 254 nm and the pH was maintained at 3 or 5 for 4 hours. The results indicated mineralization of most of the organic pollutants in waste water at lower concentrations.

III. MATERIALS AND METHODS

3.1 Catalyst Preparation

Sol-gel method : A known amount of citric acid and ethylene glycol (AR) were mixed well by keeping it over a magnetic stirrer for 10 minutes around 150° C and to this the dissolved nitrate solutions of $La(NO_3)_3.6H_2O$, $Cr(NO_3)_3.9H_2O$, $Ba(NO_3)_2$ and $Ce(NO_3)_3.6H_2O$,$Cr(NO_3)_3.9H_2O$, $Ba(NO_3)_2$of appropriate mole ratios were added and stirred for 30 minutes and the mixture was heated to 150°C till powder form is obtained.All pure single and mixed oxides were prepared by following the same procedure [7,8].Citric acid, Lanthanum, Cerium were taken in the 3:1 ratio and different mole ratios of Cr and Ba in the compounds are shown in **Table.1**

Table1. Different mole ratios of La/Ce, Cr and Ba in $MCr_{1-x}Ba_xO_{3-\delta}$

S. No	Compounds	Ratios of Cr and Ba in the compound			Sample Code
		M (La / Ce)	Cr	Ba	
1	$LaCrO_3$	1	1	0	LCBO-1

2	$LaCr_{0.4}Ba_{0.6}O_{3-\delta}$	1	0.4	0.6	LCBO-2
3	$LaBaO_{3-\delta}$	1	0	1	LCBO-3
4	$CeCrO_3$	1	1	0	CCBO-4
5	$CeCr_{0.4}Ba_{0.6}O_{3-\delta}$	1	0.4	0.6	CCBO-5
6	$CeBaO_{3-\delta}$	1	0	1	CCBO-6

3.2 Photo degradation Test for dyes

3.2.1 Photo degradation of Methyl orange

50mg of methyl orange was made up to 50 ml in a standard flask and 0.03g of $MCr_{1-x}Ba_xO_{3-\delta}$ (M=La and Ce) catalysts were added and stirred in a magnetic stirrer for 5 hrs. Then the solutions were irradiated underultra violet lightfor two days. The absorption spectra of the irradiated dye solutions were recorded for 24 hrs and 48 hrs after centrifugation.

3.2.2 Photo degradation of Eriochrome Black-T

100mg of EBT was made up to 50ml in a standard flask and 0.03g of $MCr_{1-x}Ba_xO_{3-\delta}$ (M=La and Ce) catalysts were added and stirred in a magnetic stirrer for 5 hrs. Then the solutions were irradiated under ultra violet light for two days.The absorptionspectra of the irradiated dye solutions were recorded for 24 hrs and 48 hrs after centrifugation.

IV RESULTS AND DISCUSSIONS

4.1 Powder X-Ray Diffraction Studies of catalysts

The powder XRD patterns of LCBO-2 and CCBO-5 are shown inFig. 1.The XRD patterns of LCBO-2 was compared and studied with the reported XRD patterns of $LaCrO_3$ and $LaBaO_{3-\delta}$. The $LaCrO_3$ (JCPDS- 75- 0441) is simple cubic system with 'a' value 3.880Å and $LaBaO_{3-\delta}$ (JCPDS -42- 1500) is an orthorhombic system with a = 10.66Å, b = 12.64Å and c = 3.703Å. The XRD pattern of LCBO-2 is not reported but it matches with the XRD patterns of $LaCrO_3$ and $LaBaO_{3-\delta}$with slight variation. This is due to the presence of Cr and Ba present in $LaCr_{1-x}Ba_xO_{3-\delta}$.Similarly the XRD pattern of CCBO-5 was compared and studied with the reported XRD patterns of $CeCrO_3$ and $CeBaO_{3-\delta}$.The$CeCrO_3$ (JCPDS-75- 0289) is a cubic system with 'a' value 3.890Å and $CeBaO_{3-\delta}$ (JCPDS -22- 0074) is an orthorhombic system with a = 8.779Å, b = 6.214Å and c = 6.236Å. The XRD pattern of CCBO-5 is not reported but it matches with the XRD patterns of $CeCrO_3$ and $CeBaO_3$with slight variation. This is due to the presence of Cr and Ba present in $CeCr_{1-x}Ba_xO_3$.The characteristic peaks corresponding to $MCr_{1-x}Ba_xO_{3-\delta}$ (M=La and Ce)confirms the presence of mixed metal oxideas a single phase in the compounds. Therefore, the uniqueness of these XRD patterns is a proof that the compounds LCBO-2 and CCBO-5 is of novel nature.

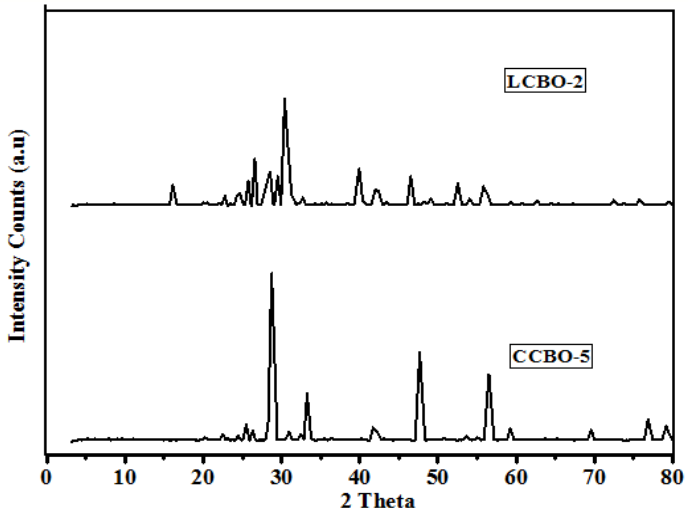
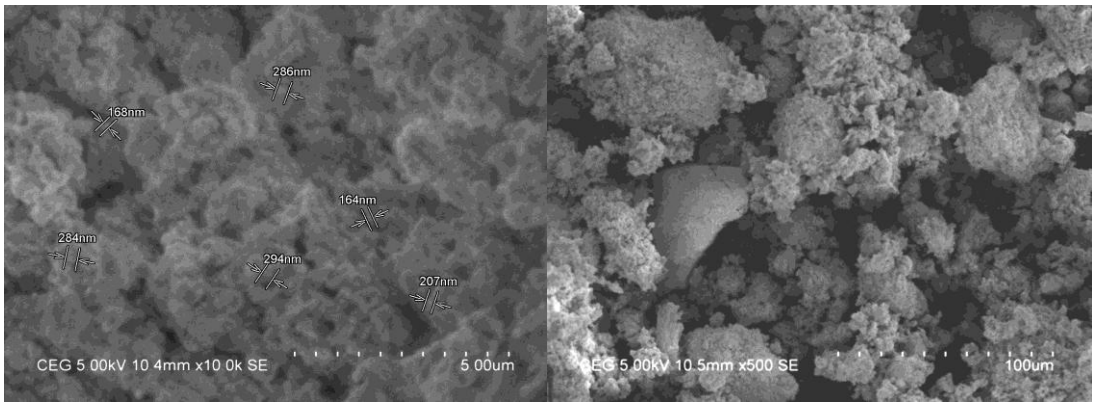


Fig. 1.XRD patterns of LCBO-2 and CCBO-5 compounds

4.2. Scanning Electron Microscopy (SEM) of catalysts

On comparing the catalytic activity of mixed metal oxides from LCBO-1 to 3 and CCBO- 4 to 6, LCBO -2 and CCBO-5 exhibited higher catalytic activity and thereby the surface morphology of these two catalysts were studied. The SEM micrographs of LCBO-2and CCBO-5are shown in Fig.2.The particle size of LCBO-2 is found to be 160-300 nm whereas the particle size of CCBO-5 is 130-270 nm. Among LCBO-2 and CCBO-5, a larger grain size, decrease in particle size and a well developed porosity is observed in CCBO-5 which plays a very important role in catalytic studies.



LCBO-2 **CCBO -5**

Fig.2.SEM micrographs of LCBO-2 and CCBO-5 compounds

4.3 FT-IR Spectroscopy of catalysts

The FT-IR spectra of LCBO-1 to LCBO-3 and CCBO-4 to CCBO-6 (Fig.3 and Fig.4)compounds exhibit a common broad band near 3400 cm^{-1} due to the OH stretching vibrations of free and hydrogen-bonded hydroxyl groups and an absorption at 1630 cm^{-1} is assigned to the deformative vibration of water molecules which is most probably due to water adsorption during the compaction of the powder specimens with KBr [7, 8]. The metal–oxygen stretching frequencies are in the range of 400–1000 cm^{-1}. The frequencies at 496.97 & 651.52; 858.54 &873.84; 936.03 cm^{-1}corresponds to La-O,Ba-O and Cr-O in the compound. The frequencies at 413.54 & 635.34; 871.66 &898.86; 934.68 cm-1 corresponds to Ce-O, Cr-O and Ba-O bonds which are existing as mixed metal oxides.On comparing the FT-IR spectrums of the compounds , it is evident that the bands near 3400 cm^{-1} and 1600 cm^{-1} indicates that the adsorption of water on the surface is more in LCBO-2 and CCBO-5 than in other compounds [7,8].

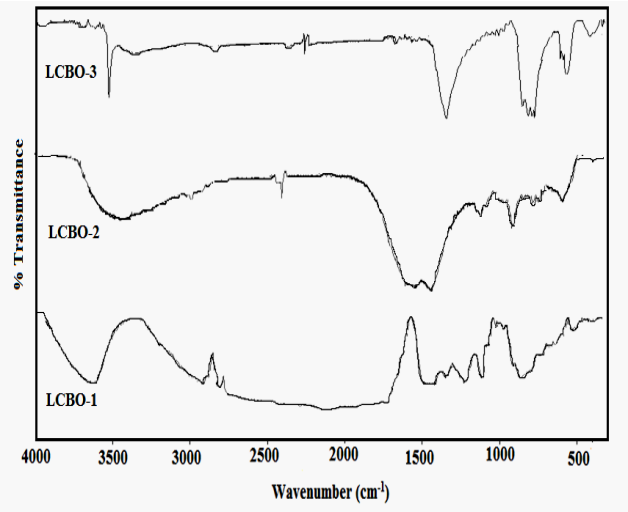


Fig.3. FT-IR Spectra of LCBO-1 to LCBO-3 compounds

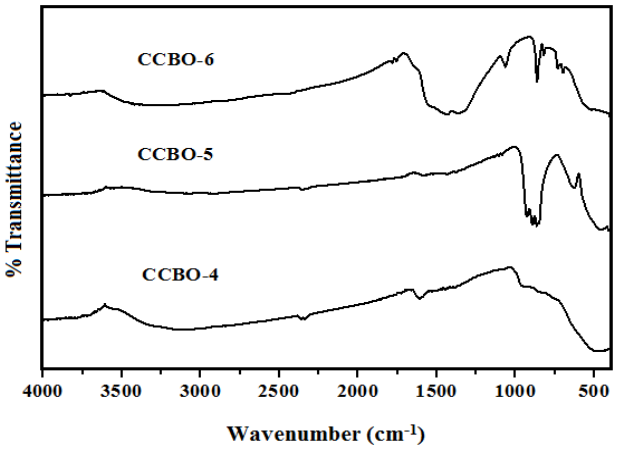


Fig.4.FT-IR spectra of CCBO-4 to CCBO-6 compounds

4.4Thermogravimetric Analysis (TGA) of catalysts

Thermal analysis was done for LCBO-2 and CCBO-5 compounds before sintering the sample in order to study the complete decomposition of impurities present in the compound. It is shown in Fig.5, that the study of the thermograms of the compounds gives an idea for fixing the sintering temperature. It has been found that the compounds were stable above 750°C and hence, the sintering temperatures of the compounds were chosen as 800°C.

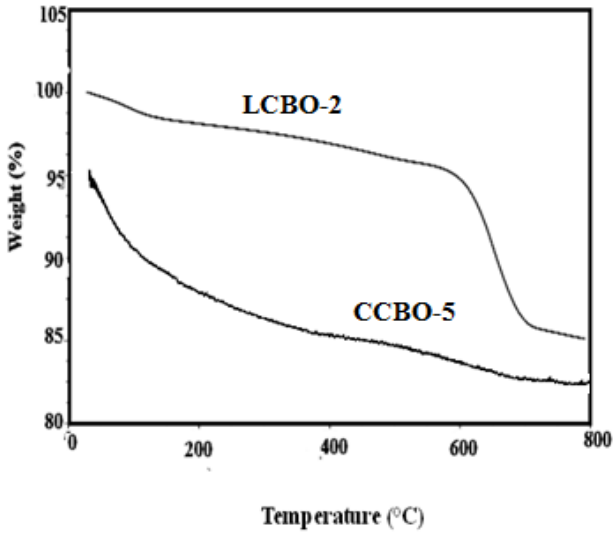


Fig.5.Thermograms of LCBO-2 & CCBO-5 before sintering

4.5 UV- Visible studies on photo-degradation of dyes with catalysts

The UV- visible absorption spectra of dyes with and without catalysts (LCBO-2 and CCBO-5) are shown in (Fig.7,8 and Fig.10,11) and the corresponding photographs of degraded dyes are shown in ((Fig.6 and Fig.9). Among the different mole ratios of mixed metal oxides (Table 1) which were prepared, LCBO-2 and CCBO-5 exhibits catalytic activity whereas LCBO-1, LCBO-3, CCBO-4 and CCBO-6 does not show catalytic activity.

The maximum wavelength observed for methyl orange and EBT solutionsare 461nm and 300 nmin the absence of catalyst, on irradiation with the UV light for 24 and 48 hours.This matches with the theoretical λ_{max} values of dyes which prove that no degradation has taken place. In the presence of catalysts (LCBO-2 and CCBO-5)dye solutions on irradiating in the UV light for 24 and 48 hours, shows a decrease in the intensity of color and change in their λ values (Table 2). This change in the absorbance values indicates the degradation of dyes.

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Table. 2. Methyl orange solution irradiated with UV light in the presence of Catalysts

S. No	Duration (Hrs)	Methyl orange Absorption bands (nm)		EBT Absorption bands (nm)	
		LCBO-2	CCBO-5	LCBO-2	CCBO-5
1.	24	192 & 462	204,272 & 458	244, 301 & 370	235,300 & 370
2.	48	212 & 374	207, 269,379 & 456	241,299 & 369	242, 297 & 369

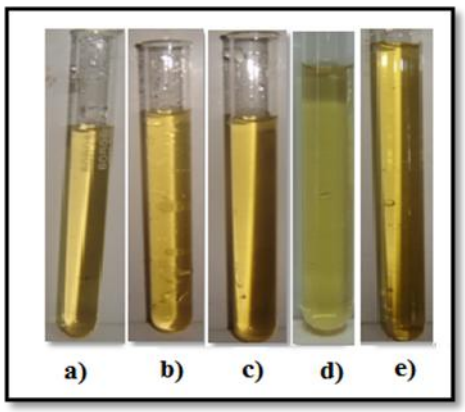

Fig.6.Photographs of
a)Methyl orange solution
b) & c) Methyl orange solution + LCBO-2 (2 Hrs & 48 Hrs)
d) & e) Methyl orange solution + CCBO-5 (24 Hrs & 48 Hrs)

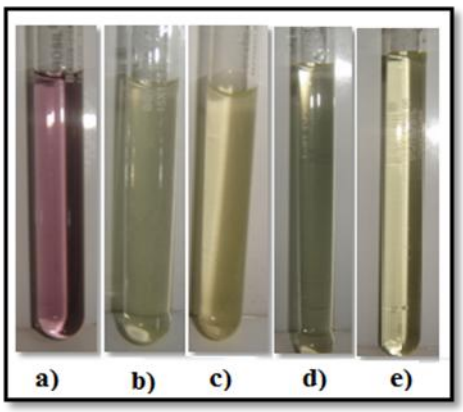

Fig.7.Photographs of
a) EBT solution
b) & c) EBT solution + LCBO-2(24 Hrs & 48 Hrs)
d) & e) EBT solution + CCBO-5(24 Hrs & 48 Hrs)

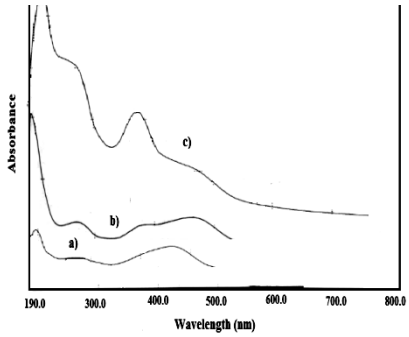

Fig. 8. UV- visible spectra of
a) Methyl orange
b) Methyl orange+LCBO-2(24 Hrs)
c) Methyl orange +LCBO-2(48 Hrs)

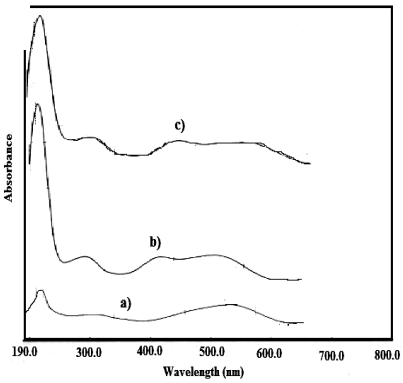

Fig. 9. UV- visible spectra of
a) Methyl orangeb) Methyl orange+CCBO-5 (24 Hrs)
c) Methyl orange +CCBO-5 (48 Hrs)

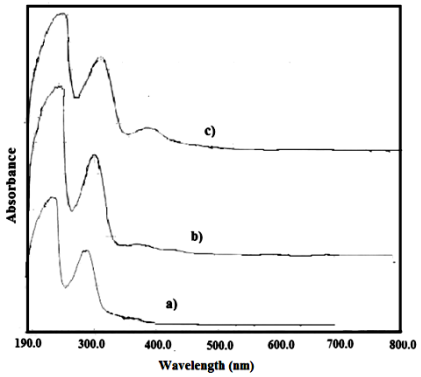

Fig. 10. UV- visible spectra of
a) EBT
b) EBT+LCBO-2 (24 Hrs)

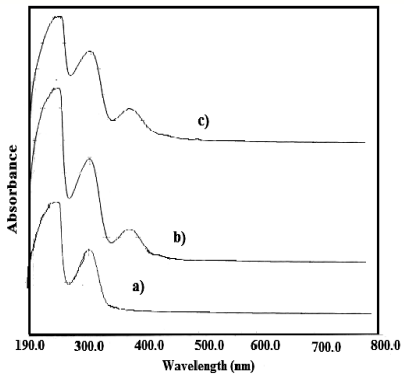

Fig. 11. UV- visible spectra of
a) EBT
b) EBT+CCBO-5 (24 Hrs)

On comparing the UV absorption studies of the dyes in the presence of catalysts, it has been observed that the photo degradation of EBT solutions has responded well than the methyl orange solutions.

VI. CONCLUSION

The photo catalytic efficiency of nano mixed metal oxide of $MCr_{1-x}Ba_xO_{3-\delta}$ were studied using methyl orange and EBT dye solutions, by irradiating the dye solutions under UV lightfor 24 and 48 hours. The irradiated dye solutions were subjected to UV- visible spectrometer to observe the changes in the absorption bands of dye solutions. The UV-visible absorption studies, has clearly shown that the EBT dye has undergone photo-degradation more effectively than methyl orange solution in the presence of nano mixed metal oxide catalysts. On comparing the different mole ratios of lanthanum and cerium based mixed metal oxide ($MCr_{1-x}Ba_xO_{3-\delta}$) cerium based mixed metal oxide ($CeCr_{0.4}Ba_{0.6}O_{3-\delta}$) has a very good catalytic efficiency towards photo degradation of dyes than lanthanum. The cerium based mixed metal oxide has high potential in future to remove the dye pollutants in effluents from dyeing industry.

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