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SYNTHESIS, CHARACTERISATION AND USE OF $LaCrO_4$ AS PHOTOCATALYST

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ABSTRACT

Photocatalysis has been established as an emerging technology for wastewater treatment since photocatalytic activity of number of semiconducting materials has already been established. For a number of chemical reactions, ternary oxides have been used as photocatalysts. In the present investigation, ternary oxide of lanthanum has been synthesized using co-precipitation. Synthesized catalyst has been characterised using X-ray diffraction patterns. Photocatalytic bleaching of methylene blue using lanthanum's ternary oxide was observed spectrophotometrically. The effect of variation of different parameters like concentration of methylene blue, pH, amount of semiconductor and light intensity was observed on the rate of photocatalytic bleaching. A tentative mechanism for the photocatalytic bleaching of methylene blue has been proposed.

Key words: Lanthanum chromium oxide, Methylene blue, Calcination, Semiconductor, Photocatalytic bleaching.

INTRODUCTION

For the treatment of wastewater, photocatalysis has became a promising method all over the globe. It is being used for solving the problem of environmental pollution and even has remedial effect from harmful bacteria as reported by Toshiyuki *et al.*[1]. The field of photocatalysis has been extensively searched by many photochemists. Lea and Adesina[2] reported the photooxidative degradation of sodium dodecyl sulphate in aerated aqueous TiO_2 suspensions. Blajeni *et al.*[3] reported the photoreduction of CO_2 and water into HCHO and CH_3OH in aqueous suspension of $SrTiO_3$, WO_3 and TiO_2. Lehn *et al.*[4] reported the photochemical decomposition of water by UV irradiation on rhodium loaded $SrTiO_3$ catalysts. The mechanism of gas-phase dehydration of cyclohexanol and methyl

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cyclohexanols catalysed by zirconium phosphate and zirconium phosphite was proposed by Costa et al.[5]. The use of zirconium and germanium phosphates in heterogeneous photocatalytic oxidation of naphthalenes to phthalic anhydride was reported by Monaci and Ginestra[6]. Kawai *et al.*[7] reported the synthesis of conjugated oligo (silylene-vinylene) by metathesis of divinylsilanes over $Re_2O_7 - Al_2O_3$ catalyst. Reddy and Ganesh[8] studied the characterisation of La_2O_3 and V_2O_5 / $La_2O_3 - TiO_2$ catalysts and their activity for synthesis of 2,6-dimethyl phenol. Cateno *et al.*[9] reported the structure activity relationship of lanthanide doped V_2O_5/Al_2O_3 catayst. Lopez *et al.*[10] studied the synthesis, characterisation and catalytic properties of $Pt/CeO_2 - Al_2O_3$ and $Pt/La_2O_3 - Al_2O_3$ sol gel derived catalyst. Tascon *et al.*[11] prepared, characterized and tried to find out the catalytic properties of $LaMeO_3$ oxides (here Me denotes 3d-metals). Domen *et al.*[12] investigated the photocatalytic decomposition of water vapours on $SrTiO_3$ powder impregnated with NiO. The photocatalysis of water on illuminated $SrTiO_3$ was investigated by Yoneyama *et al.*[13]. Domenech and Andres[14] reported the photoreduction of Hg (II) ions in aqueous suspensions of TiO_2 and WO_3. The photocatalytic decomposition of steam over TiO_2 and $RuO_2 - TiO_2$ surfaces was reported by Kawai and Sakata[15]. In the present work, ternary oxide of lanthanum was synthesized, characterized and used as a photocatalyst for the degradation of methylene blue, which is extensively used in textile industries.

EXPERIMENTAL

Synthesis of ternary oxide of lanthanum by co-precipitation

Lanthanum chromium oxide was prepared by co-precipitation of their hydroxides from a mixture of aqueous solution of chromium nitrate and lanthanum nitrate by the addition of ammonium hydroxide solution. The procedure is as follows: Required quantities of $La(NO_3)_3.6H_2O$ and $Cr(NO_3)_3.9H_2O$ were dissolved separately in distilled water (50.0 mL.) to prepare 0.4 M solution of each and then both these solutions were mixed. Aqueous ammonium hydroxide solution was added rapidly to the mixed nitrate solutions at room temperature, where a dark green coloured precipitate was formed. The pH of the solution was maintained at 7.5, which ensured complete co-precipitation of La and Cr ions as their hydroxides.

Heat treatment

The precipitate along with the supernatant solution was kept in an oven at 110° C for 15-16 hours for drying. The dried precipitate was subjected to stepwise calcinations by heating from 150°C to terminal temperature 725°C. For the heat treatment, the dried precipitate was heated in the muffle furnace with increase in the temperature at a rate of 10° C per minute from one temperature to the subsequent higher temperature. After heating at 600°C for 12 hours, the material was furnace cooled and grounded in acetone in a gap of 6 hours, using a pastel and mortar. Later on the ground material was further heated at 650°C for 12 hours. At this temperature also, it is grounded in acetone twice in a gap of 6 hours. Now the material is finally heated at 725°C for 5 hours. The calcination at 725°C was completed without in between grinding of the material. Calcination temperature and heating schedule during heat treatment of lanthanum chromium oxide is given in Table 1.

Table 1. Calcination temperature and heating schedule

Temperature (ºC)	Duration (hrs)
150	0.5
200	0.5
225	0.5
250	0.5
300	1.0
350	1.0
400	2.0
450	2.0
500	3.0
550	3.0
600	12.0
650	12.0
725	5.0

XRD characterization

The prepared ternary oxide was characterized by X-ray diffraction method. Fig. 1 present the X-ray diffraction patterns of $LaCrO_4$ synthesized from the co-precipitation of $La(NO_3)_3.6H_2O$ and $Cr(NO_3)_3.9H_2O$ in hydroxide forms and calcined at terminal temperatures of 600°C, 650°C and 725°C for different periods. Fig. 1 shows the characteristic peaks from $2\theta = 25.5°$ to 79.9°, which corresponds well with $LaCrO_4$ stoichiometry X-ray patterns. The stoichiometry of the ternary oxide sample has been established with the help of published diffraction data file - JCPDS (Joint Committee on Powder Diffraction Standards). Since values are known from JCPDS files, they are matched with the 2θ values obtained from the sample.

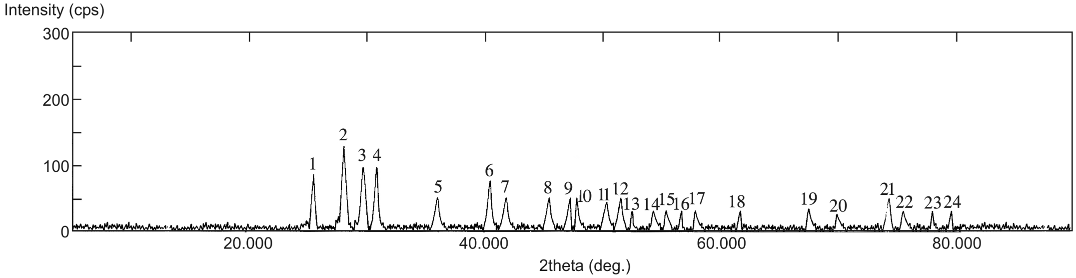

Fig. 1

In Fig. 1, the graph has been plotted between intensity (cycles per second) and 2θ values in degrees. For general consideration, we had taken the 2θ value ranging from 20.0° to 80.0°, where the occurrence of peaks were observed, which are numbered from 1 to 24. On comparing the X-ray patterns, it was concluded that there is a maximum possibility of phase having $LaCrO_4$ stoichiometry.

Table 2. XRD data

Peak No.	2 theta (2θ)	FWHM	d-value	Intensity	I/I_o
1	25.5	0.235	9.8173	84	63
2	27.2	0.235	9.3017	132	100
3	29.2	0.235	9.0176	99	74
4	30.5	0.235	8.3128	99	74
5	36.3	0.235	8.2176	50	41
6	41.1	0.235	7.3298	76	70
7	42.0	0.235	7.215	50	41
8	45.8	0.235	7.0157	51	42
9	49.7	0.235	6.3921	51	42
10	50.0	0.235	6.2168	50	41

Cont…

Peak No.	2 theta (2θ)	FWHM	d-value	Intensity	I/I_o
11	53.1	0.235	6.1094	48	39
12	53.8	0.235	6.0236	50	41
13	54.0	0.235	5.9124	37	25
14	55.2	0.235	5.8793	36	24
15	56.1	0.235	5.7872	36	24
16	57.3	0.353	5.6389	36	24
17	58.1	0.353	5.4321	37	25
18	62.7	0.353	5.3976	37	25
19	67.3	0.353	5.2174	37	25
20	69.8	0.353	5.1293	31	21
21	74.8	0.353	5.0171	52	43
22	75.4	0.353	4.8106	33	23
23	78.9	0.235	4.7132	32	22
24	79.9	0.235	4.6179	32	22

Experimental procedure for photocatalytic bleaching of methylene blue

Methylene blue and lanthanum chromium oxide were used in the present investigation. The solution of methylene blue dye (MB) was prepared in doubly distilled water. The photocatalytic bleaching of methylene blue was studied in the presence of semiconducting lanthanum chromium oxide catalyst and light. 0.0374 g of methylene blue was dissolved in 100 mL. of double distilled water so that the concentration of dye solution was 1.0 x 10^{-3} M. This solution was used as a stock solution. The photocatalytic bleaching of the dye was observed using different concentrations of the dye and semiconductor at different pH and light intensities. The irradiation was carried out keeping the whole assembly under light.

A 200 watt tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by Suryamapi (CEL model SM 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of previously standardized 0.1N sulphuric acid (Rankem, 98%) and 0.1N sodium hydroxide (Rankem, 97%) solutions. The necessary condition for the correct measurement of optical density is that the solution must be free from semiconductor particles and other impurities. A U.V-VIS spectrophotometer (Systronics Model 108) was used for measuring absorbance at different time intervals.

RESULTS AND DISCUSSION

The photocatalytic bleaching of methylene blue in presence of lanthanum chromium oxide semiconductor at different time intervals was observed at λ_{max} 665 nm. For typical run, the pH was taken as 8.7, the concentration of methylene blue was 1.20×10^{-5} M, the amount of semiconductor was taken as 0.10 g. and the intensity of light radiation was kept 60.0 mW cm^{-2}. The results for a typical run are graphically represented in the Fig. 2. It was observed that absorbance of methylene blue solution decreases with the increase in the time of irradiation thus, indicating that methylene blue is photocatalytically degraded on irradiation (control experiments were also performed, which indicated that dye degrades only in the presence of photocatalyst and light).

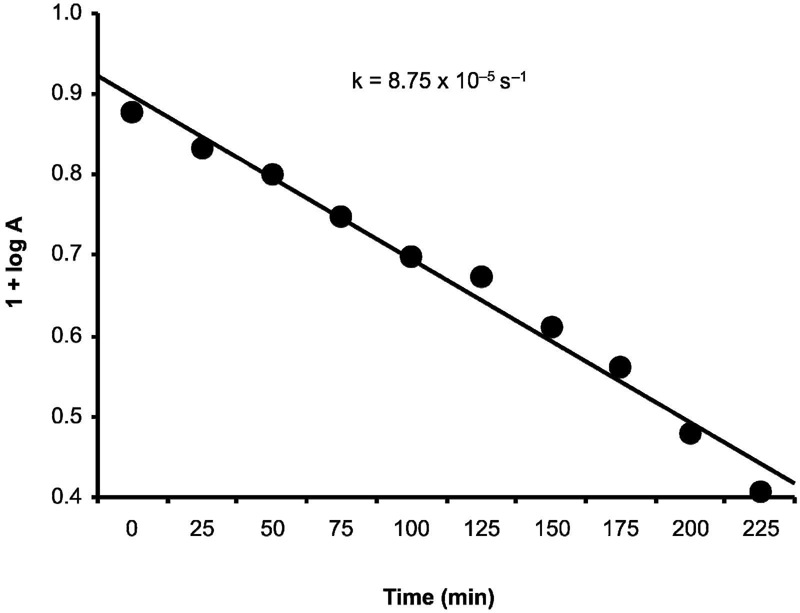

Fig. 1: A typical run

A plot of 1 + log A versus time was linear and followed pseudo first order kinetics.

The rate constant was measured using following expression:

$$k = 2.303 \times \text{slope}$$

Effect of pH

The effect of pH on the rate of photocatalytic bleaching of methylene blue was investigated in the pH range (7.1-9.5). It is evident from the data that the rate of photcatalytic bleaching of methylene blue increases with increase in pH. The increase in the rate of photcatalytic bleaching may be due to more availability of the OH ions at higher pH values. These OH ions will generate more OH radicals by combining with holes. These hydroxide radicals are considered responsible for this photcatalytic bleaching. But after a certain value of pH (pH = 8.7), a further increase in the pH of the medium decreases the rate of photocatalytic bleaching. It may be due to the fact that the dye does not remains in its cationic form due to greater concentration of OH ions and as such, the reaction rate decreases. The results are reported in the Table 3.

Effect of variation of dye concentration

Effect of variation of dye concentration was also studied by taking different concentrations of methylene blue. It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of dye. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with an increase in the concentration of dye, further. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic bleaching of methylene blue. The results are given in Table 3.

Effect of amount of lanthanum chromium oxide

The amount of photocatalyst is also likely to affect the rate of dye bleaching. Here different amounts of photocatalysts were used. It has been observed that initially the rate of bleaching of methylene blue increases with an increase in the amount of semiconductor but ultimately it becomes almost constant after a certain amount (0.10 g). This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductor was increased further, there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point; above which, any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of methylene blue. As any increase in the amount of semiconductor after saturation point will only increase the thickness of the layer at the bottom of the vessel, once the complete bottom of the reaction vessel is covered by the photo catalyst. The results are reported in Table 3.

Effect of light intensity

To observe the effect of intensity of light on the photocatalytic bleaching of methylene blue, the distance between the light source and the exposed surface area of reaction mixture was varied. The intensity of light at each distance was measured by Suryamapi (CEL Model SM 201). The bleaching action was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. The rate of photocatalytic bleaching was increased upto 60.0 $mWcm^{-2}$. The decrease in the rate beyond 60.0 $mWcm^{-2}$ may be due to thermal effects caused by increase in intensity. The results obtained are given in Table 3.

MECHANISM

On the basis of the observed data, the following tentative mechanism may be proposed for the photocatalytic bleaching of methylene blue (MB).

$$ {}^{1}MB_{0} \xrightarrow{h\nu} {}^{1}MB_{1} \text{ (singlet)} \qquad ...(1) $$

$$ {}^{1}MB_{1} \xrightarrow{h\nu} {}^{3}MB_{1} \text{ (triplet)} \qquad ...(2) $$

$$ LaCrO_{4} \xrightarrow{h\nu} LaCrO_{4}\,[h^{+}\,(VB) + e^{-}\,(CB)] \qquad ...(3) $$

$$ {}^{3}MB_{1} + LaCrO_{4}\,[h^{+}\,(VB) + e^{-}\,(CB)] \longrightarrow MB^{+} + LaCrO_{4}\,e^{-}\,(CB) \qquad ...(4) $$

$$ LaCrO_{4}\,[e^{-}\,(CB)] + O_{2} \longrightarrow LaCrO_{4} + O_{2}^{\bullet -} \qquad ...(5) $$

$$ MB^{+} + OH^{-} \longrightarrow MB + {}^{\bullet}OH \qquad ...(6) $$

$$ MB + {}^{\bullet}OH \longrightarrow \text{Colourless products} \qquad ...(7) $$

Table 3. Effect of variation of different parameters

Effect of pH		**Effect of azure-B concentration**		**Effect of amount of $LaCrO_4$**		**Effect of intensity of light**	
[MB] = 1.20 x 10^{-5} M		pH = 8.7		pH = 8.7		pH = 8.7	
LaCrO4 = 0.10 g		LaCrO4 = 0.10 g		[MB] = 1.20 x 10^{-5} M		[MB] = 1.20 x 10^{-5} M	
Light Intensity = 60.0 mWcm^{-2}		Light Intensity = 60.0 mWcm^{-2}		Light Intensity = 60.0mWcm^{-2}		LaCrO4 = 0.10 g	
Temperature = 306 K		Temperature = 306 K		Temperature = 306 K		Temperature = 306 K	
pH	**Rate constant x 10^5 (s^{-1})**	**[MB] x 10^5 M**	**Rate constant x 10^5 (s^{-1})**	**Amount of LaCrO4 (g)**	**Rate constant x 10^5 (s^{-1})**	**Light intensity (mWcm^{-2})**	**Rate constant x 10^5 (s^{-1})**
7.1	7.73	0.6	7.6	0.02	7.89	20	8.07
7.5	7.93	0.8	7.99	0.04	8.11	30	8.24
7.9	8.14	1	8.18	0.06	8.32	40	8.41
8.3	8.34	**1.2**	**8.75**	0.08	8.53	50	8.58
8.7	**8.75**	1.4	8.37	**0.1**	**8.75**	**60**	**8.75**
9.1	7.93	1.6	8.18	0.12	8.75	70	8.58
9.5	7.73	1.8	7.79	0.14	8.75	80	7.74
–	–	–	–	0.16	8.75	–	–

When the solution of the dye was exposed to light in the presence of a semiconductor, initially the methylene blue molecules are excited to their first singlet state. These excited singlet molecules are converted to their triplet state through inter system crossing (ISC). The triplet state may donate its electrons to the semiconductor and the methylene blue becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor, thus, regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of methylene blue will immediately react with hydroxyl ions to form OH radicals and these OH radicals will oxidize the methylene blue molecule into colorless products. The participation of OH radicals as an active oxidizing species was confirmed by carrying out the reaction in the presence of hydroxyl radical scavenger e.g; 2-propanol, where the reaction rate was drastically retarded.

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