Int. J. Chem. Sci.: 9(2), 2011, 941-948
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS AND CHARACTERIZATION OF La_2NiO_4 AND ITS USE IN PHOTOCATALYTIC DEGRADATION OF YELLOWISH ORANGE DYE

PARAMJEET KAUR, NEELAM GANDHI and R. C. KHANDELWAL*

Department of Chemistry, B. N. P. G. College, UDAIPUR – 313001 (Raj.) INDIA

ABSTRACT

Ternary oxides have been used as effective photocatalysts in carrying out a number of chemical reactions. In the present work, lanthanum nickel oxide catalyst has been prepared using microwave heating. It has been characterized by XRD. Photocatalytic degradation of yellowish orange dye has been observed using this catalyst and progress of reaction has been monitored spectrophotometrically. The effect of variation of different parameters i.e. pH, amount of La_2NiO_4, concentration of yellowish orange and light intensity was studied. A tentative mechanism for photocatalytic degradation of yellowish orange has been proposed.

Key words: Ternary oxides, La_2NiO_4, Photocatalytic degradation, Yellowish orange.

INTRODUCTION

Photocatalysis has become an emerging technology for treatment of waste water all over the world. Photoreduction of CO_2 and water into formaldehyde and methanol on aqueous suspension of $SrTiO_3$ and TiO_2 was investigated by Blajaeni et al.[1] Photodegradation of dye pollutants on one dimensional TiO_2 nanoparticles under UV and visible irradiation was investigated by Chen et al.[2] Wang et al.[3] studied photocatalytic degradation and kinetics of orange-G using nano sized Sn (IV) - TiO_2 as a photocatalyst. Mansoori et al.[4,5] used zinc oxide and lead oxide (PbO) as photocatalyst for the photocatalytic bleaching of rhodamine-B and rhodamine-6G. Tang et al.[6] investigated the photocatalytic decomposition of the organic pollutants by Bi_2WO_6 under visible light irradiation. Generally binary chalcogenides (especially oxides and sulphides) are being used as photocatalyst. Luo et al.[7] studied the structure and redox properties of $Ce_xPr_{1-x}O_2$ delta mixed oxides and their catalytic activities for CO, CH_3OH and CH_4 combustion. The search for new photocatalyst has led to the present study of ternary oxides. The use of ternary oxide

---

*Author for correspondence

like $SrTiO_3$ is limited as its λ_{max} falls in the near U.V. or at the border of visible range. Chaudhary et al.[8] performed carbon free dry reforming of methane to syngas over $NdCoO_3$ perovskite type mixed metal oxide catalyst. Therefore, extensive research has been carried out using 3d-transition metal ions for the preparation of ternary oxides including perovskites. Tascon et al.[9] prepared, characterized and tried to find out the catalytic properties of $LaMO_3$ oxides. (Here M denotes 3d-metals). Novio et al.[10] observed partial or complete heterogeneous photocatalytic oxidation of toluene and 4-picolene in liquid organic oxygenated dispersions containing pure and iron doped titania photocatalyst. These synthesized ternary oxides have been used in photobleaching of dyes.

Looking to the importance of photocatalyst for pollution control, there is a need to synthesize some newer photocatalysts. The synthesis, characterization and photocatalytic activity of lanthanum chromium oxide ($LaCrO_3$) catalyst was reported by Jose et al.[11].

In the present work, lanthanum nickel oxide (La_2NiO_4) was synthesized, characterized and used as a photocatalyst for degradation of yellowish orange, which is extensively used in dyeing industries.

EXPERIMENTAL

Synthesis of photocatalyst

La_2NiO_4 was prepared by co-precipitation of metal nitrates upon addition of ammonium hydroxides. 0.2 M aqueous solution (100 mL) of Ni $(NO_3)_2.6H_2O$ was added to 0.2 M aqueous solution (100 mL) of La $(NO_3)_3.6H_2O$. Aqueous NH_4OH solution was added rapidly to the mixed nitrate solutions at room temperature. The pH of solution was maintained at 8.5 for complete co-precipitation of La and Ni ions as their hydroxides. The filtered precipitate was kept for drying in an oven at 60°C for 24 hrs. Dried precipitate was grounded with the help of mortar and pestle. The grounded material was then irradiated with microwave radiations for 6 min. The synthesized ternary oxide was then washed with dil. acetic acid to separate unreacted La_2O_3 and NiO.

Materials and method

1.0×10^{-3} M solution of yellowish orange (0.2262 g of yellowish orange in 500 mL water) was prepared in doubly distilled water. This solution was used as a stock solution. The irradiation was carried out keeping the whole assembly under light. For irradiation purpose, a 200 W tungsten lamp (Philips) was used. The intensity of light was measured at various distances by Solarimeter (CEL model SM 201). The pH of the solution was measured by a digital pH meter (Systronics 335). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The optical density was measured by a U.V. spectrophotometer (Systronics Model 106).

RESULTS AND DISCUSSION

The photocatalytic degradation of yellowish orange in presence of La_2NiO_4 at different time intervals was observed at λ_{max} 480 nm. A cut off filter was placed outside the beaker to remove any thermal radiations and to ensure illumination by visible light only. The change in O.D. versus time was observed at regular intervals. The rate constant for this reaction was determined using the expression:

$$k = 2.303 \times \text{slope} \qquad \ldots(1)$$

For typical run set-up, the pH was taken 7.0, the concentration of yellowish orange was taken 1.66×10^{-5} M, the amount of La_2NiO_4 was taken 0.3 g and the intensity of light radiation was taken 70.0 mW/cm^2. The typical run has been presented in Fig. 1. It has been observed that absorbance of yellowish orange solution decreases with the increase in time of radiation. This indicates that yellowish orange is photocatalytically degraded on irradiation.

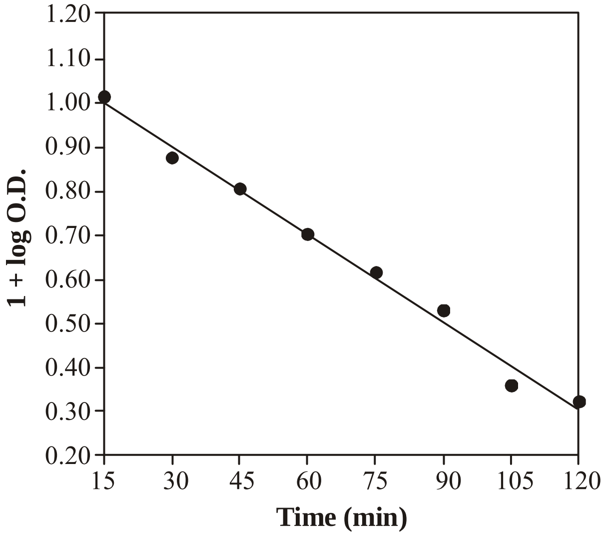

Fig. 1: A typical run

A plot of 1 + log O.D versus time was linear and follows pseudo-first order kinetics.

Characterization of La_2NiO_4

The prepared La_2NiO_4 was characterized by X-ray diffraction method. The X-ray diffraction pattern of La_2NiO_4 has been shown in Fig. 2. The graph has been plotted between intensity and 2θ values in degrees (2θ value ranges from 20°-80°).

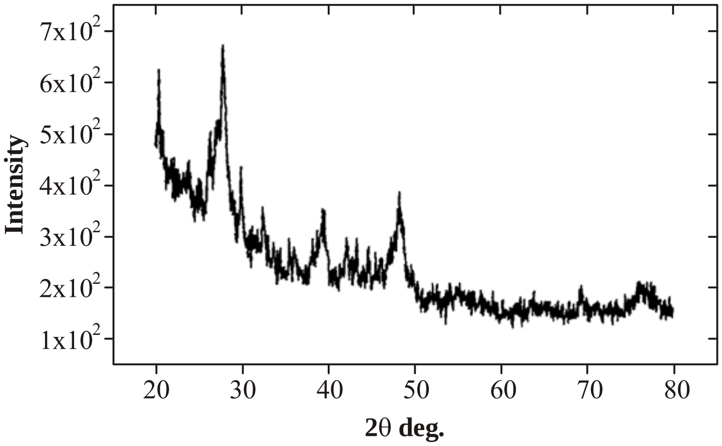

Fig. 2 X-ray diffraction pattern of La_2NiO_4

Effect of pH

The effect of pH on the rate of photocatalytic degradation of yellowish orange was investigated in the range of 6.0- 8.5. The rate of degradation of yellowish orange increases with increase in pH up to 7.0 and above this pH, there is a decrease in the rate of photocatalytic degradation of yellowish orange. It may be explained on the basis that at low pH photocatalyst remains positively charged and the dye molecules (almost in neutral form) are not attracted by the photocatalyst. But at higher values of pH, the surface of photocatalyst become negatively charged due to greater concentration of OH ions and the dye in its anionic form will face a force of repulsion and as such rate of reaction decreases. The results are reported in Table 2.

Effect of amount of semiconductor

The amount of semiconductor also affects the rate of degradation of dye. The effect of variation of amount of semiconductor was studied by taking different amounts of La_2NiO_4 (0.15 g - 0.4 g).

It has been observed that initially the rate of degradation of yellowish orange increases with an increase in amount of semiconductor but it becomes almost constant after a certain amount (0.3 g). It may explained on the basis that as the amount of photocatalyst was increased, the exposed area also increases and hence, more active sites were available on the surface of photocatalyst for striking of photons, resulting in formation of more electron-hole pairs by absorption of light. But after a certain limit, increase in amount of photocatalyst only increases the thickness of layer, as the bottom of the reaction vessel was already covered by photocatalyst. The results are reported in Table 2.

Table 1: A typical run

[Yellowish orange] = 1.66 x 10^{-5} M [La_2NiO_4] = 0.3 g
Light intensity = 70 mW/cm^2 pH = 7.0

Time (min.)	Optical density (O.D.)	1+ log O.D.
15	1.018	1.007
30	0.754	0.877
45	0.636	0.803
60	0.504	0.702
75	0.410	0.612
90	0.338	0.528
105	0.230	0.361
120	0.210	0.322
		k = 2.52 x 10^{-4} sec^{-1}

Effect of concentration of yellowish orange

The effect of variation of dye concentration was studied by taking different concentrations of yellowish orange (0.83 x 10^{-5} M - 5.0 x 10^{-5} M).

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye up to 1.66 x 10^{-5} M. This can be explained on the basis that as the concentration of yellowish orange was increased, more dye molecules were available for excitation and consecutive degradation and hence, an increase in rate of reaction was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be due to the fact that the dye started acting as a filter for the incident light and it would not permit the desired light intensity to reach semiconductor surface; thus, decreasing the rate of degradation of yellowish orange. The results are reported in Table 2.

Table 2: Effect of variation of different parameters

Effect of pH		**Effect of amount of La_2NiO_4**	
[Yellowish orange] = 1.66 x 10^{-5}M Light intensity = 70.0 mW/cm^2 La_2NiO_4 = 0.3 g		pH = 7.0 [Yellowish orange] = 1.66 x 10^{-5}M Light intensity = 70.0 mW/cm^2	
pH	**Rate constant x 10^4 (s^{-1})**	**Amount of La_2NiO_4 (gm)**	**Rate constant x 10^4 (s^{-1})**
6.0	1.40	0.15	0.82
6.5	2.00	0.20	1.93
7.0	2.52	0.25	2.06
7.5	2.38	0.30	2.52
8.0	2.26	0.35	2.37
8.5	1.93	0.40	1.94

Effect of yellowish orange concentration		**Effect of intensity of light**	
pH = 7.0 Light intensity =70.0 mW/cm^2 La_2NiO_4 = 0.3 g		pH = 7.0 [Yellowish orange] = 1.66 x 10^{-5} M La_2NiO_4 = 0.3 g	
[Yell. org.] x 10^5 M	**Rate constant x 10^4 (s^{-1})**	**Light intensity (mW/cm^2)**	**Rate constant x 10^4 (s^{-1})**
0.83	2.40	30.0	1.65
1.66	2.52	40.0	1.87
2.50	2.05	50.0	2.13
3.33	1.69	60.0	2.22
4.16	1.22	70.0	2.52
5.00	1.15	-	-

Effect of light intensity

The effect of light intensity was studied by changing the distance between light source and the exposed surface of area (30.0 mW/cm^2 – 70.0 mW/cm^2).

The degradation 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. However, higher intensities were avoided assuming that it may cause thermal effects. The results are reported in Table 2.

Mechanism

On the basis of experimental observations, the following tentative mechanism may be proposed for the photocatalytic degradation of yellowish orange dye.

$$^{1}\mathrm{Dye}_0 \xrightarrow{hv} {}^{1}\mathrm{Dye}_1 \quad \ldots(2)$$

$$^{1}\mathrm{Dye}_1 \xrightarrow{I\mathrm{SC}} {}^{3}\mathrm{Dye}_1 \quad \ldots(3)$$

$$\mathrm{SC} \xrightarrow{hv} \mathrm{SC}^{*}\,[h^{+}\,(\mathrm{VB}) + e^{-}\,(\mathrm{CB})] \quad \ldots(4)$$

$$^{3}\mathrm{Dye}_1 + e^{-} \longrightarrow {}^{3}\mathrm{Dye}_1^{-}\ (\text{Leuco form}) \quad \ldots(5)$$

$$^{3}\mathrm{Dye}_1^{-}\ (\text{Leuco form}) \longrightarrow \text{Colourless products} \quad \ldots(6)$$

When the solution of dye was exposed to light in presence of semiconductor, initially the yellowish orange molecules are excited first to their excited singlet state. These excited singlet molecules are converted to the triplet state through inter system crossing (ISC). Semiconductor also utilizes radiant energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This electron present in conduction band may be utilized to reduce the dye in its leuco form, which ultimately degrades to colorless products. The reaction rate is not affected in the presence of hydroxyl radicals scavenger 2-propanol. Thus no oxidation takes place and the dye is reduced by the electron.

ACKNOWLEDGEMENT

Authors are thankful to Dr. Mukul Gupta and Mr. Aamir, UGC-DAE-CSR, Indore for providing the XRD facilities and Head, Department of Chemistry, B. N. P. G. College, Udaipur for providing laboratory facilities. The authors are also grateful to Dr. Suresh C. Ameta for providing necessary technical help.

REFERENCES

1. B. A. Blajeni, M. Halmann and J. Manassen, Solar Energy, **25**, 165 (1980).

2. J. Y. Li and W. H. Ma Chen, J. Mol. Catal., **2619**, 131 (2007).
3. J. H. Sin, X. L. Wang and J. Y. Sun, J. Mol. Catal., **260**, 235 (2006).
4. R. A. Mansoori, S. Kothari and R. Ameta, J. Indian Chem. Soc., **81**, 335 (2004).
5. R. A. Mansoori, S. Kothari and R. Ameta, Arabian J. Sci. Eng., **11**, 29 (2004).
6. J. W. Tang, Z. G. Zous and J. H. Ye, Catal. Lett., **92**, 53 (2004).
7. M. F. Luo, Z. L. Yan and L. Y.,Jin, J. Mol. Catal. A-Chem., **260(1-2)**, 157 (2006).
8. V. R. Chaudhary, K. C. Mondal and A. S. Mamman, Catal. Lett., **100**, 271 (2005).
9. M. D. Tascon, S. Mendioroz and L. G. Tejuca, Z. Physik. Chem., **124S**, 109 (1981).
10. J. A. Novio, M. G. Gomery, M. A. P Adrian and J. F. Moto, J. Mol. Catal., **8**, 101 (1996).
11. J. Jose, J. Ameta, P. B. Punjabi, V. K. Sharma and S. C. Ameta, Bull. Catal., Soc. India, **6**, 110 (2007).

Revised : 08.04.2011 *Accepted : 10.04.2011*