Acta Chimica
&
Pharmaceutica Indica

Acta Chim. Pharm. Indica: 4(2), 2014, 97-103
ISSN 2277-288X

ROLE OF BISMUTH VANADATE AS A PHOTOCATALYST FOR THE REDUCTION OF MALONIC ACID

ABHILASHA TRIPATHI, SURBHI BENJAMIN, DIPTI SONI and SURESH C. AMETA*

Department of Chemistry, PAHER Univerity, UDAIPUR – 313003 (Raj.) INDIA

(*Received : 24.03.2014; Accepted : 05.04.2014*)

ABSTRACT

The photocatalytic reduction of malonic acid was carried out in presence of bismuth vanadate and visible light. The effect of various parameters like pH, concentration of malonic acid, amount of bismuth vanadate and light intensity has been studied. A tentative mechanism has been proposed for photocatalytic reduction of malonic acid involving bismuth vanadate as a photoreductant. The product was characterized as a mixture of aldehyde and alcohol.

Key words: Photocatalytic reduction, Bismuth vanadate, Malonic acid.

INTRODUCTION

Water pollution is a burning problem all over the globe, which requires some eco-friendly methods for its purification. Researchers have developed some methods for wastewater treatment like adsorption, electrolyte decomposition, ion exchange method, biological methods etc. These treatment methods are not suitable at large scale due to high cost and therefore, some alternative methods are required, which are reliable as well as green chemical in nature. Photocatalysis provides an eco-friendly pathway for degradation of many organic pollutants. This technique is considered as a promising technology for wastewater treatment.

Photochemistry plays a vital role in a number of biological and chemical processes. Photocatalysis[1] is "A catalytic reaction involving light absorption by a substrate. Similarly, the substrate, which absorbs light and acts as a catalyst for the chemical reaction is known as photocatalyst. Rare are the examples, where reduction can be carried out by a semiconductor in the presence of light. Bismuth vanadate is one of such a photocatalyst, which can reduce an organic compound. It may provide a green chemical pathway for reduction, which is also an energy storage reaction.

World is facing problems of global warming as well as energy crisis. Both these problems can be solved to a reasonable extent by photoreduction of carbon dioxide[2]. $BiVO_4$ powder was synthesized by a hydrothermal method[3,4]. Liu et al.[5] reported selective ethanol formation from photocatalytic reduction of carbon dioxide in water with $BiVO_4$ photocatalyst. Bi_2O_3-ZrO_2 was found to be more photoactive than Bi_2O_3,

---

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: ameta_sc@yahoo.com

ZrO_3, TiO_2 and ZnO for the reduction of Cr(VI)[6]. Li et al.[7] reported that the degradation of phenol can be carried out by porous Ag/$BiVO_4$ film under visible light. The Ag/AgI/Bi_2WO_6 photocatalysts were successfully synthesized by deposition-precipitation and photoreduction methods by Gui et al.[8]

Iliev et al.[9] reported the degradation of oxalic acid in aqueous solution photocatalyzed by TiO_2 modified with nanosized gold particle. The analytical application of the photochemical reduction of ferric sulphate in sunlight by oxalic and lactic acid was studied by Gopala et al.[10] Photoreduction of oxalate vanadyl (IV) complex in aqueous solution of oxalic acid has also been reported[11]. The photocatalytic performance of the as prepared Au/$BiVO_4$ have also been evaluated via mineralization of oxalic acid and malonic acid under visible light irradiation[12]. The reduction of Hg(II) by small semivolatile dicarboxylic acids (C_2-C_4) was observed by Si et al.[13]

Malonic acid is a dicarbooxylic acid with structure $CH_2(COOH)_2$. The ionized form of malonic acid, as well as its ester and salts are known as malonates. Its molar mass is 104.06 $gmol^{-1}$ and it is miscible with water.

EXPERIMENTAL

Preparation of bismuth vanadate

Materials

Bismuth (III) nitrate pentahydrate, ammonium metavanadate, nitric acid (70%), ammonium hydrogen carbonate, oxalic acid and malonic acid.

Synthesis of $BiVO_4$

$BiVO_4$ was synthesized through precipitation method. 0.1 M bismuth (III) nitrate pentahydrate solution was mixed with 0.1 M of ammonium metavanadate solution and stirred continuously at room temperature until a clear yellow solution was obtained. The solution was titrated with ammonium hydrogen carbonate to induce precipitation. The precipitate formed was filtered and washed several times with distilled water and dried in oven at 60ºC overnight. The precipitate obtained was calcined at 450ºC[14].

Characterization

To determine the phase composition of the sample powder, X-ray diffraction analysis was carried out using Shimadzu XRD-6000 diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5406 A), over the 2θ range of 20-60º. According to Yu et al.[15], the crystal structure of monoclinic scheelite $BiVO_4$ is much similar to that of tetragonal scheelite, except for some distortion.

The XRD of the product is given below in Fig. 1. The product formed is monoclinic in nature as a ≠ b ≠ c (a = 7.146 Å, b = 6.873 Å, c = 5.974 Å,) and the angle (α = β = 90˙ and y ≠ 90). The size of the crystal was calculated by Sherrer formula is 363 nm and cell volume is 293.4 Å.

0.20 g Malonic acid was dissolved in 100.0 mL of doubly distilled water so that the concentration of solution was 0.01 M. 50 mL solution of malonic acid (0.01 M) was taken and 0.10 g of bismuth vanadate was added to it. The pH of the reaction mixture was adjusted to 4.0 and then this solution was exposed to a 200 W tungsten lamp at 50.0 $mWcm^{-2}$.

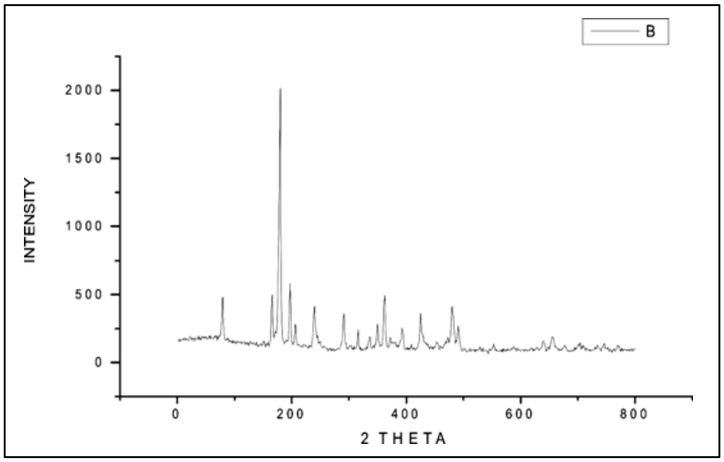


Fig. 1

Aliquot (2 mL) of reaction mixture was taken and titrated against standardized sodium hydroxide solution using phenolphthalein as an indicator at regular time intervals. The plot of log V versus time was found to be linear, which indicated that the reaction follows first order. The rate constant was measured by the relation –

$$k = 2.303 \text{ x slope} \qquad \ldots(3.1)$$

The results are reported in Table 1.

Table 1: A typical run

pH = 4.0 Bismuth vanadate = 0.10 g

[Malonic acid] = 1.00×10^{-2} M Light Intensity = 50.0 $mWcm^{-2}$

Time (min.)	Volume (V) (mL)	log V
0.0	3.50	0.5441
30.0	3.35	0.5250
60.0	3.25	0.5119
90.0	3.10	0.4914
120.0	2.90	0.4624
150.0	2.85	0.4548
180.0	2.70	0.4314
210.0	2.60	0.4150
240.0	2.50	0.3979

Rate constant (k) = 2.52×10^{-5} sec^{-1}

Effect of pH

The pH of the solution is likely to affect the reduction of malonic acid. The effect of pH on the rate of reduction of malonic acid was investigated in the pH range 1.5 - 4.5. The results are reported in Table 2.

Table 2: Effect of pH

[Malonic acid] = 1.00 × 10^{-2} M Light intensity = 50.0 $mWcm^{-2}$
Bismuth vanadate = 0.10 g

pH	Rate constant (k) × 10^5 (sec^{-1})
1.5	0.93
2.0	0.99
2.5	1.75
3.0	1.87
3.5	1.99
4.0	**2.52**
4.5	1.77

Effect of malonic acid concentration

Effect of variation of malonic acid concentration was also studied by taking different concentrations of malonic acid i.e. 0.25-33.3 x 10^{-2} 0.33 M. The results are tabulated in Table 3. It is evident from the observed data that the rate of photocatalytic reduction increases with increasing concentration of the malonic acid. The rate constant was found optimum at 0.01 M and thereafter, it decreases on increasing the concentration of malonic acid further.

Table 3: Effect of concentration malonic acid

pH = 4.0 Light intensity = 50.0 $mWcm^{-2}$
Bismuth vanadate = 0.10 g

[Malonic acid] × 10^2 M	Rate constant (k) × 10^5 (sec^{-1})`
0.25	1.12
0.50	1.76
0.75	2.03
1.00	**2.52**
5.00	1.98
6.25	1.46
8.00	1.43
11.00	1.37
12.50	1.20
14.20	1.16
20.00	0.93
33.00	0.89

Effect of amount of bismuth vanadate

The amount of semiconductor also affects the process of reduction of acid. Different amounts of photocatalyst were used (0.02 to 0.16 g). The results are given in Table 4.

Table 4: Effect of amount of bismuth vanadate

pH = 4.0 Light intensity = 50.0 $mWcm^{-2}$
[Malonic acid] = 1.00×10^{-2} M

Amount of $BiVO_4$ (g)	Rate constant (k) × 10^5 (sec^{-1})
0.02	1.10
0.04	1.71
0.06	1.77
0.08	2.07
0.10	**2.52**
0.12	2.50
0.14	2.54
0.16	2.52

Effect of light intensity

The effect of the variation of light intensity on the rate was also investigated by changing the distance between light source and surface of the semiconductor. The observations are summarized in the Table 5.

Table 5: Effect of light intensity

pH = 4.0 Bismuth vanadate = 0.10 g
[Malonic acid] = 1.00×10^{-2} M

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^5 (sec^{-1})
20.0	1.47
30.0	1.68
40.0	1.75
50.0	**2.52**
60.0	2.13

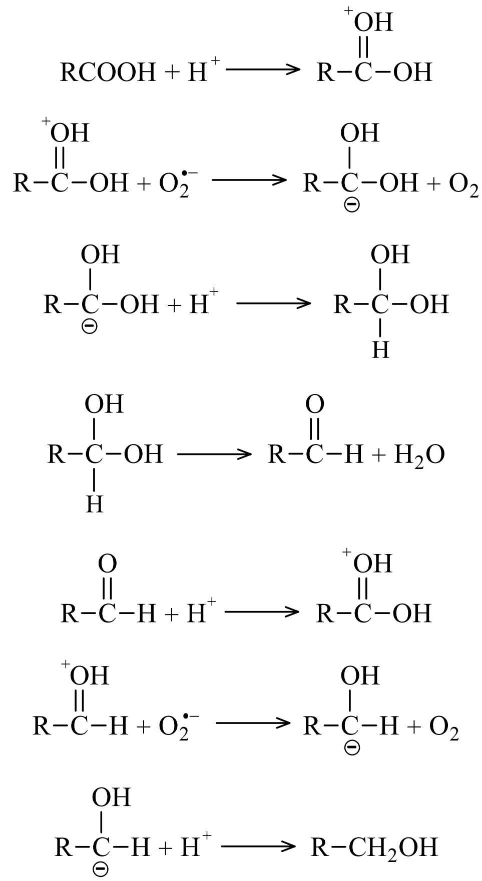
The reduction of malonic acid was confirmed by performing group test of an aldehyde and alcohol in the reaction mixture exposing it for 4 hrs. It gives positive test of aldehydic and alcoholic groups while test of carboxylic acid was negative as it does not give any effervescence with a saturated solution of sodium bicarbonate.

Mechanism

Based on experimental observations, a tentative mechanism for the reduction of acids was proposed as –

$$SC \xrightarrow{h\nu} SC^* \quad ...(2)$$

$$SC^* + O_2 \text{ (Dissolved oxygen)} \xrightarrow{h\nu} O_2^{\bullet -} + SC^+ \quad ...(3)$$



...(4) …(5) ...(6) ...(7) ...(8) ...(9) ...(10)

where R = CH_2COOH

REFERENCES

1. IUPAC Glossary of Terms used in Photochemistry Pure Appl. Chem., **60**, 1055-1106 (1988).

2. R. Ameta, S. Panchal, N. Ameta and S. C. Ameta, Photocatalytic Reduction of Carbon Dioxide, Materials Science Forum, **764**, 83-96 (2013).

3. Q. Chen, M. Zhou, D. Ma and D. Jing, Effect of Preparation Parameter on Photoactivity of $BiVO_4$ by Hydrothermal Method, J. Nanomaterial, Art No. 621254 (2012).

4. P. Pookmanee, K. Pingmunag, S. Phanichphat and W. Kangwansupamonkon, J. Microscopy Soc., **23(1)**, 95-98 (2009).

5. Y. Liu, B. Huang, Y. Dai, X. Zhang, X. Qin, M. Jiang and M.- H. Whangbo, Selective Ethanol Formation from Photocatalytic Reduction of Carbon-dioxide in Water with $BiVO_4$ Photocatalyst, Catal. Comm., **11(3)**, 210-213 (2009).

6. K. Vignesh, R. Priyanka, M. Rajarajan and A. Suganthi, Photoreduction of Cr(VI) in Water using Bi_2O_3- ZrO_2 Nanocomposite under Visible Light Irradiation, Mater. Sci. Engg. B: Solid-State Mater. Adv. Technol., **178(2)**, 149-157 (2013).

7. X. Q. Li, X. F. Zhang, X. L. Dong, C. Ma, X. X. Zhang and H. C. Ma, Fabrication of Porous Ag/$BiVO_4$ Film for Efficient Degradation of Phenol under Visible Light, Adv. Mater. Res., **518-523**, 732-735 (2012).

8. M. S. Gui, P. F. Wang, M. M. Tang and D. Yuan, Plasmon-Induced Photodegradation of Toxic Pollutants with $Ag/Agl/Bi_2WO_6$ under Visible-Light Irradiation, Adv. Mater. Res., **807-809**, 1534-1542 (2013).

9. V. Iliev, D. Tomova, L. Bilyarska and G. Tyuliev, Influence of the Size of Gold Nanoparticles Deposited on TiO_2 upon the Photocatalytic Destruction of Oxalic Acid., J. Mol. Catal., **263(1-12)**, 32-38 (2007).

10. G. R. Gopala, G. Aravamudan and C. N. Venkatamma, Estimation of Ferric Salts through Photochemical Reduction with Oxalic and Lactic Acids, Fres. Z. Anal. Chem., **146(3)**, 161-166 (1955).

11. A. Matsumoto, H. Kumafuji and J. Shiokawa, Photoreduction of Oxalato Vanadyl (IV) Complex in Aqueous Solution of Oxalic Acid, Inorg. Chim. Acta, **51** (C), 213-215 (1981).

12. K. Pingmuang, N. Wetchakun, W. Kangwansupamonkon, K. Ounnunkad, B. Inceesungvorn and S. Phanichphant, Photocatalytic Mineralization of Organic Acids over Visible-Light-Driven $Au/BiVO_4$ Photocatalyst, Int. J. Photoenergy, **2013** Article ID 943256 (2013).

13. L. Si and A. P. Ariya, Reduction of Oxidized Mercury Species by Dicarboxylic Acid (C_2-C_4): Kinetics and Product Studies, Envron. Sci. Tech., **42(14)**, 5150-5155 (2008).

14. A. H. Abdullah, N. M. Ali and M. I. M. Tahir, Synthesis of Bismuth Vanadate as Visible-Light Photocatalyst, Malaysian J. Anal. Sci., **13(2)**, 151-157 (2009).

15. J. Yu, Y. Zhang and A. Kudo, Synthesis and Photocatalytic Performance of $BiVO_4$ by Ammonia Co-Precipitation Process, J. Solid State Chem., **182**, 223-228 (2009).