Scientific Reviews & Chemical Communications

Sci. Revs. Chem. Commun.: 4(2), 2014, 55-60

ISSN 2277-2669

PHTOCATALYTIC ACTIVITY OF FORMIC ACID IN PRESENCE OF BISMUTH VANADATE

ABHILASHA TRIPATHI, SANYOGITA SHARMA[a], PARAS TAK and SURESH C. AMETA[*]

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

[a]Department of Chemistry, Pacific Institute of Technology, UDAIPUR – 313003 (Raj.) INDIA

(*Received : 29.03.2014; Accepted : 07.04.2014*)

ABSTRACT

The photocatalytic reduction of formic acid was carried out in presence of bismuth vanadate visible using light as the source of energy. The effect of various parameters like pH, concentration of formic acid, amount of bismuth vanadate and light intensity on the rate of photocatalytic reduction was observed. A tentative mechanism has been proposed for photocatalytic reduction of formic acid involving bismuth vanadate as a photoreductant.

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

INTRODUCTION

Sun is the principal source of energy in nature and it helps in the production of energy rich compounds required for sustenance of life. Photochemistry plays a vital role in a number of biological and chemical processes. Photochemical processes are of the greatest importance for life on earth. Interesting enough, $BiVO_4$ can be used as a photocatalytic reductant with a difference that other semiconductor are mainly used as an oxidant. It may provide a green chemical pathway for reduction, which is also an energy storage reaction. CuO/TiO_2 photocatalysts were prepared and shown to enhance the rate of CO_2 photoreduction and the production of total organic carbon (TOC), including HCOOH, HCHO and CH_3OH[1]. Raja et al.[2] reported that the formation of formic acid is one of the products as evident from cyclic voltammetry and confirmed using chromatographic analysis. Aman et al.[3] studied a range of hole scavengers, where EDTA (ethylenediaminetetraacetic acid) and formic acid are found to be the most active for the reduction reaction. Reduction of CO_2 to different products, including CO, formic acid, and methanol was investigated by Kumar et al.[4] Photocatalytic reduction to synthetic organic fuels like formaldehyde, methanol, formic acid, acetic acid, methane, etc. will provide a solution to the problem of energy crisis as it will give us alternate fuels, which can be burnt into fuel cells to generate electricity[5]. Shkrob et al.[6] have observed that formic acid and its derivatives can be reduced to the formyl radical via a concerted reaction, while the electron transfer is coupled to oxygen transfer to a Ti^{3+} center on the oxide surface. The effects on TiO_2 (Degussa P25) photocatalytic reduction of Cr(VI) under visible light, using methanol, methanal and Formic acid as electron donors were investigated by Zhang et al.[7] Transient absorption and electron paramagnetic resonance (EPR) spectroscopies were used to study reactions of photogenerated electrons and

---

Available online at www.sadgurupublications.com

[*]Author for correspondence; E-mail: ameta_sc@yahoo.com

holes on TiO_2. Methanol, formaldehyde, and formic acid have been observed in the photocatalytic reduction of CO_2.[8] Mishra et al.[9] studied the high nitrate reduction with formic acid and attributed it to the formation of CO_2 species having high reduction potential. The Pt/Si/Ag diodes also show high activity for photoconversion of formic acid into carbon dioxide and hydrogen[10]. Teramura[11] reported that photocatalysis is a promising method for converting other carbon sources such as carbon monoxide (CO), formaldehyde (HCHO), formic acid (HCOOH), methanol (CH_3OH), and methane (CH_4). The photoreduction process of Cu(II) in presence of formic acid was aimed to clarify the reaction mechanism and assess the reaction kinetics by Canterino et al.[12] The formic acid-mediated photoreduction of aromatic nitro compounds in room temperature acetonitrile solutions was investigated by Cors et al.[13] The photodeposition of cadmium selenide (CdSe) using Se-TiO_2 photocatalysts at pH 3.5 and 7 in the presence of formic acid was studied by Nguyen et al.[14] The photocatalytic formation of formic acid and formaldehyde were measured spectrophotometrically using Nash reagent by Jain et al.[15] Premkumar and Ramaraj[16] studied the photocatalytic reduction of carbon dioxide to formic acid at porphyrin and phthalocyanine adsorbed nafion membranes

Formic acid is also called methanoic acid and it is the simplest carboxylic acid. Its chemical formula is HCOOH. It is an important intermediate in chemical synthesis and occurs naturally, most notably in ant venom. Its name comes from the Latin word for ant i.e. formica, referring to its early isolation by the distillation of ant bodies. Esters, salts and the anions derived from formic acid are referred to as formates. It is used in regenerating old rubber and reduces dyeing of wool fast colors. Its molar mass is 46.03 g/mol and it is miscible with water.

EXPERIMENTAL

2.12 mL of formic acid was dissolved in 100.0 mL of doubly distilled water so that the concentration of solution was 0.05 M. 50 mL solution of formic acid (0.05 M) was taken and 0.10 g of bismuth vanadate was added to it. The pH of the reaction mixture was adjusted to 5.0 and then this solution was exposed to a 200 W tungsten lamp at 50.0 $mWcm^{-2}$.

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 (3.1).

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

The results are reported in Table 1.

Table 1: A typical run

pH = 5.0 Bismuth vanadate = 0.10 g

[Formic acid] = 5.00×10^{-2} M Light intensity = 50.0 $mWcm^{-2}$

Time (min.)	Volume (V) (mL)	1 + log V
0.0	1.50	1.1761
30.0	1.10	1.0414
60.0	0.95	0.9777
90.0	0.80	0.9031

Cont…

Time (min.)	Volume (V) (mL)	1 + log V
120.0	0.70	0.8450
150.0	0.60	0.7782
180.0	0.50	0.6990
210.0	0.45	0.6532
240.0	0.40	0.6021
		Rate constant (k) = 8.15×10^{-5} sec^{-1}

Effect of pH

The pH of the solution is likely to affect the reduction of formic acid. The effect of pH on the rate of reduction of formic acid was investigated in the pH range 1.5-5.5. The results are reported in Table 2.

Table 2: Effect of pH

[Formic acid] = 5.00×10^{-2} M   Light intensity = 50.0 $mWcm^{-2}$
Bismuth vanadate = 0.10 g

pH	Rate constant (k) × 10^5 (sec^{-1})
1.5	1.59
2.0	1.76
2.5	1.88
3.0	1.99
3.5	2.25
4.0	2.47
4.5	3.44
5.0	**8.15**
5.5	6.02

Effect of formic acid concentration

Effect of variation of formic acid concentration was also studied by taking different concentrations of formic acid i.e. 0.01 M to 0.125 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 formic acid. The rate constant was found optimum at 0.05 M and thereafter, it decreases on increasing the concentration of formic acid further.

Table 3: Effect of formic acid concentration

pH = 5.0   Light intensity = 50.0 $mWcm^{-2}$
Bismuth vanadate = 0.10 g

[Formic acid] × 10^2 M	Rate constant (k) × 10^5 (sec^{-1})
1.00	3.22
2.00	5.97

Cont…

[Formic acid] × 10^2 M	**Rate constant (k) × 10^5 (sec^{-1})**
5.00	**8.15**
7.50	6.27
8.00	3.88
11.10	2.16
12.50	0.87

Effect of amount of bismuth vanadate

The amount of semiconductor also affects the process of acid reduction. 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 = 5.0 Light intensity = 50.0 $mWcm^{-2}$
[Formic acid] = 5.00 × 10^{-2} M

Amount of $BiVO_4$ (g)	**Rate constant (k) × 10^5 (sec^{-1})**
0.02	1.67
0.04	2.01
0.06	3.40
0.08	5.21
0.10	**8.15**
0.12	8.13
0.14	8.11
0.16	8.10

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 = 5.0 Bismuth vanadate = 0.10 g
[Formic acid] = 5.00 × 10^{-2} M

Light intensity ($mWcm^{-2}$)	**Rate constant (k) × 10^5 (sec^{-1})**
20.0	1.72
30.0	3.47
40.0	5.33
50.0	**8.15**
60.0	4.27

The reduction of formic acid was confirmed by performing usual group test of an aldehyde and alcohol in the reaction mixture after 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.

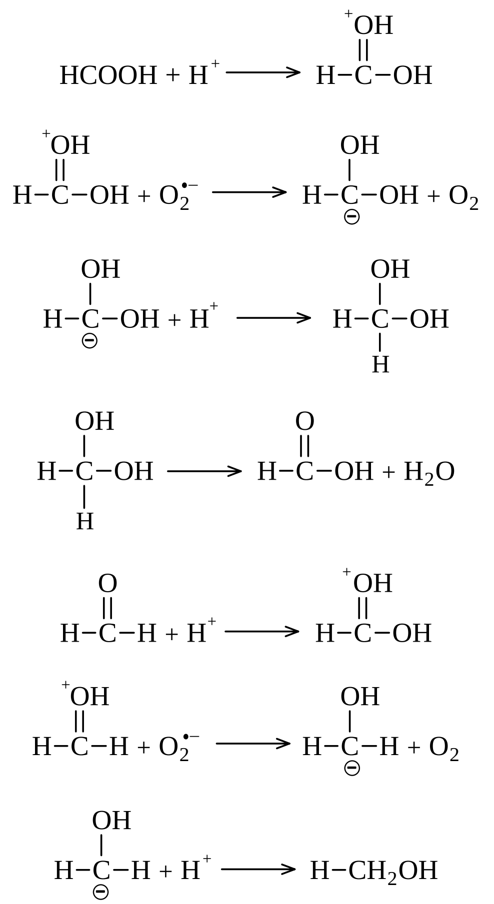
The products were confirmed by GC-MS of the sample of the reaction mixture after exposing it to the light 10 hours. The results of GC-MS indicate the formation of formaldehyde as the major product and methanol in traces.

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)

REFERENCES

1. X. Yang, T. Xiao and P. P. Edwards, The Use of Products from CO_2 Photoreduction for Improvement of Hydrogen Evolution in Water Splitting, Int. J. Hydrogen Energy, **36(11)**, 6546-6552 (2011).

2. K. S. Raja, Y. R. Smith, N. Kondamudi, A. Manivannan, M. Misra and V. Subramanian, CO_2 Photoreduction in the Liquid Phase over Pd-Supported on TiO_2 Nanotube and Bismuth Titanate Photocatalysts, Electrochem. Solid State Lett., **14(5)**, F5-F8 (2011).

3. N. Aman, T. Mishra, J. Hait and R. K. Jana, Simultaneous Photoreductive Removal of Copper (II) and Selenium (IV) under Visible Light over Spherical Binary Oxide Photocatalyst, J. Hazard. Mater., **186(1)**, 360-366 (2011).

4. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, Photochemical and Photoelectrochemical Reduction of CO_2, Ann. Rev. Phys. Chem., **63**, 541-569 (2012).

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

6. I. A. Shkrob, N. M. Dimitrijevic, T. W. Marin, H. He and P. Zapol, Heteroatom-Transfer Coupled Photoreduction and Carbon Dioxide Fixation on Metal Oxides, J. Phys. Chem., **C 116(17)**, 9461-9471 (2012).

7. X. Zhang, L. Song, X. Zeng and M. Li, Effects of Electron Donors on the TiO_2 Photocatalytic Reduction of Heavy Metal Ions under Visible Light, Adv. Intell. Soft Comp., **138 AISC**, 327-333 (2012).

8. N. M. Dimitrijevic, I. A. Shkrob, D. J. Gosztola and T. Rajh, Dynamics of Interfacial Charge Transfer to Formic Acid, Formaldehyde, and Methanol on the Surface of TiO_2 Nanoparticles and its Role in Methane Production, J. Phys. Chem., **C 116(1)**, 878-885 (2012).

9. T. Mishra, M. Mahato, N. Aman, J. N. Patel and R. K. Sahu, A Mesoporous WN Co-Doped Titania Nanomaterial with Enhanced Photocatalytic Aqueous Nitrate Removal Activity under Visible Light, Catal. Sci. Technol., **1(4)**, 609-615 (2011).

10. Y. Qu, T. Xue, X. Zhong, Y.-C. Lin, L. Liao, J. Choi and X. Duan, Heterointegration of Pt/Si/Ag Nanowire Photodiodes and their Photocatalytic Properties, Adv. Funct. Mater., **20(18)**, 3005-3011 (2010).

11. K. Teramura, Photoreduction of CO_2 to CO in the Presence of H_2 over Various Basic Metal Oxide Photocatalysts, ACS National Meeting Book of Abstracts (2009).

12. M. Canterino, I. Di Somma, R. Marotta and R. Andreozzi, Kinetic Investigation of Cu(II) Ions Photoreduction in Presence of Titanium Dioxide and Formic Acid, Water Res., **42(17)**, 4498-4506 (2008).

13. A. Cors, S. M. Bonesi and R. Erra-Balsells, Photoreduction of Nitro Arenes by Formic Acid in Acetonitrile at Room Temperature, Tetrahedron Lett., **49(9)**, 1555-1558 (2008).

14. V. H. H. Nguyen, R. Amal and D. Beydoun, Photodeposition of CdSe using Se-TiO_2 Suspensions as Photocatalysts, J. Photochem. Photobiol. A: Chemistry, **179(1-2)**, 57-65 (2006).

15. S. Jain, J. Vardia, R. Ameta and S. C. Ameta, Use of Malachite Green as Photocatalyst in Reduction of Sodium and Potassium Carbonates, Energy Conv. Manage., **45(7-8)**, 1233-1242 (2004).

16. J. Premkumar and R. Ramaraj, Photocatalytic Reduction of Carbon Dioxide to Formic Acid at Porphyrin and Phthalocyanine Adsorbed Nafion Membranes, J. Photochem. Photobiol. A: Chemistry, **110(1)**, 53-58 (1997).

17. 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).

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