Journal of Scientific & Industrial Research
Vol. 68, October 2009, pp. 891-893

Effect of photosensitizers and inorganic ions on hydrogen generation from hydrogen sulfide

R Priya and S Kanmani*
Centre for Environmental Studies, Anna University, Chennai 600 025, India

Received 27 January 2009; revised 25 June 2009; accepted 23 July 2009

This study presents hydrogen (H_2) generation from hydrogen sulfide (H_2S) using photocatalyst [(CdS/ZnS)/Ag_2S+(RuO_2/TiO_2)] with photosensitizers (Rhodamine B, Eosin Y, Methylene Blue and Methyl Violet). In presence of Rhodamine B, photocatalyst yields 1.3 times more H_2 than control. In presence of anions (I^-, Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-}) and cations (Fe^{3+}, Cu^{2+}), photocatalyst yields less H_2.

Keywords: Dye sensitization, Hydrogen, Hydrogen sulfide, Solar photocatalysis

Introduction

Hydrogen generation from cheap raw materials like hydrogen sulfide (H_2S) is a challenging process for future energy needs. Methods for H_2S removal are claus and wet absorption methods and thermochemical, electrochemical and photochemical processes. In photocatalysis, using colloidal semiconductors (TiO_2, CdS, ZnS, CdSe, ZnO etc.) as photocatalysts, solar energy photodecomposes H_2S. Being a promising photocatalyst, photoactivity of CdS can be improved by adding ZnS wide band gap energy semiconductor. Promoters like Ag_2S can also enhance activity in catalysts[1]. In photocatalytic H_2 generation, synthetic dyes were used as photosensitizers to sensitize wide band gap semiconductors[2].

This study presents effect of organic dyes as photosensitizers in presence of photocatalyst [(CdS/ZnS)/Ag_2S+(RuO_2/ TiO_2)] and inorganic ions on H_2 generation from H_2S.

Materials and Methods

Cadmium carbonate, silver nitrate, sodium sulfide, sodium sulfite, and titanium dioxide (Degussa, P25), zinc carbonate and ruthenium trichloride (Merek) were used. Cadmium acetate and zinc acetate were prepared by dissolving purified cadmium carbonate and zinc carbonate in acetic acid. Other chemicals used were of analytical reagent grade. Mixed semiconductor photocatalyst [(CdS/ZnS)/Ag_2S)+(RuO_2/TiO_2)] was prepared by mixing of CdS/ZnS/Ag_2S and RuO_2/TiO_2. CdS/ZnS/Ag_2S was prepared by mixing of coprecipited CdS/ZnS and Ag_2S. RuO_2/TiO_2 was prepared by incipient wetness impregnation method. Dye solutions were prepared by dissolving required quantity of dye powders of Rhodamine B (RB), Eosin Y (EY), Methylene blue (MB) and Methyl violet (MV).

Experiments were carried out in a batch (300 ml) three phase (s-l-g) photocatalytic reactor for H_2 generation. Suspensions were deaerated with N_2 for 30 min to prevent uptake of photogenerated electrons by dissolved O_2. Catalyst particles were kept suspended by magnetic stirrers. Reactor temperature was maintained by external circulation of water. Whole apparatus was placed on terrace under sunlight. Volume of H_2 was measured at 15 min interval till H_2 generation ceases. H_2 gas, collected by water displacement arrangement, was confirmed on a gas chromatograph (chromatograph and Instruments Company) with TCD using Porapak Q column at 40°C and N_2 as a carrier. Average radiation intensity measured was 422 W/m^2.

Results and Discussion

Effect of Photosensitizers

To study effect of photosensitizers on H_2 generation, experiments were conducted using organic dyes. Photocatalyst powders (75 mg) were dispersed in 0.5 M sulfide/0.25 M sulfite solution (50 ml). H_2 (38 ml) was

*Author for correspondence
E-mail: skanmani@hotmail.com, chempriya_2001@yahoo.co.in

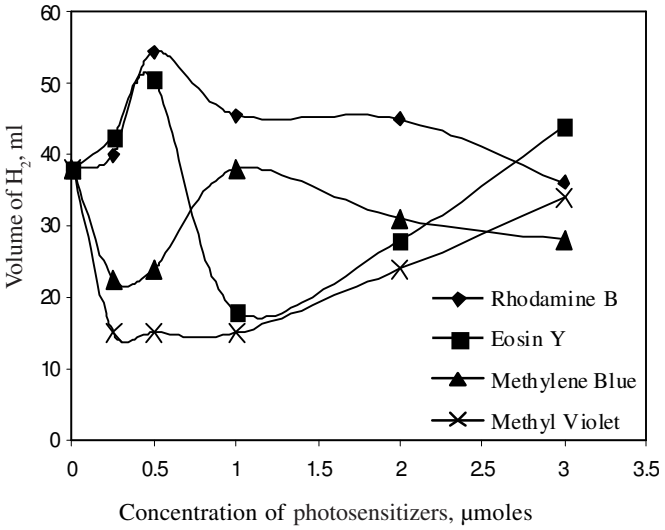

Fig. 1— Effect of photosensitizers on H_2 generation

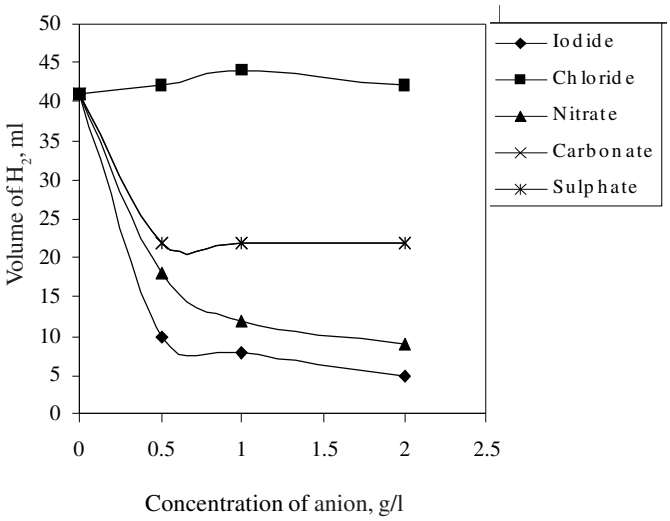

Fig. 2 — Effect of anions on H_2 generation

generated without photosensitizers or control. Concentration of organic dyes was varied (0.25-3 μm) (Fig. 1). RB dye (conc. 0.5 μm) generated maximum H_2 (54 ml), whereas RB (conc. 0.25 μm) generated only 40 ml of H_2. With increase in RB (conc. 1-2 μm), generation of H_2 decreased from 45.5 to 45 ml. Rozenkevich & Sakharovsky[3] supported increase in H_2 generation with RB.

In order to justify unadsorbed RB (conc.0.25-3 μm), a mixture of photocatalyst (75 mg) with sulfide/sulfite solution (50 ml) was shaken and allowed to stand still for 1 h. It was filtered through Whatman filter paper no. 42. Filtrate contained RB, indicating presence of unadsorbed dye in the medium. For photosensitizing action, dye is required to be adsorbed on photocatalyst. This condition was well achieved with RB, as it poses carboxyl function. With increase in dye concentration, there might be increase in RB amount adsorbed on catalyst surface. Such a linear dependence was favourable up to 0.5 μm. With further increase in RB concentration, concentration of RB in solution in bulk also increased. Hence, light absorption also increased.

Almost similar results were obtained with EY, which (conc.0.5 μm) generated maximum H_2 ion (50.5 ml). With further increase of EY (conc.1-3 μm), H_2 generation increased from 18 ml to 44 ml. Such a non-linear behavior in H_2 generation was due to different adsorption amount of EY in different catalysts[3,4].

Similarly, MB dye (conc.1 μm) generated maximum H_2 (38 ml), due to presence of free unadsorbed MB particles on adsorbed catalyst surface. MB adsorption on catalyst particles had given positive effect and free unadsorbed MB on catalyst particles had given negative effect on H_2 generation. Hence, net effect became equalizing to H_2 volume in comparison with control sample. In case of MB, structure did not pose an adsorbing sight similar to RB. Hence, there might be decrease in absorption of light on catalyst surface as compared to RB. With increase in dye concentration, there might be increase in dye adsorption. MB ions aggregated at 1 μm and left less dye ions for adsorption on catalyst surface. Hence, H_2 generation decreased. With increase in MB concentration (>1 μm), H_2 generation increased. Hence, there must be supply of some dye ions towards adsorption on catalyst surface. It accounted for increase in H_2 generation. Similar behavior was also observed for EY.

At lower concentrations (0.25-1 μm), effect of MV on H_2 generation had shown non-linear behaviour. H_2 volume generated was less (50%) than control samples, due to presence of enough free unadsorbed MV particles. At higher MV (conc.3 μm), H_2 volume generated was nearly equal to control sample, due to enough adsorption of MV on catalyst surface.

Effect of Inorganic Ions

Effect of inorganic anions [iodide (I^-), chloride (Cl^-), nitrate (NO_3^-), carbonate (CO_3^{2-}) and sulphate (SO_4^{2-})] at different concentration (0.5, 1, and 2 g/l) on H_2 generation was studied (Fig. 2) by dispersing photocatalyst powders (150 mg) in 0.5 M sulfide/ 0.25 M sulfite solution (100 ml). H_2 generation was found to decrease as follows: potassium iodide, 76-88; sodium nitrate, 78-56; sodium carbonate, 46; and sodium sulphate, 46%. Sodium chloride increased H_2 generation from 2.4% to

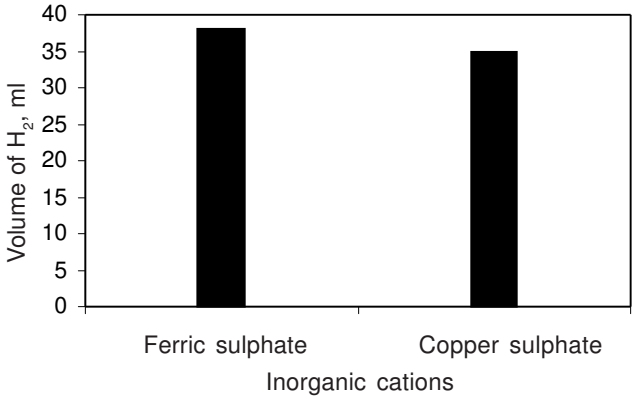

Fig. 3 — Effect of inorganic cations on H_2 generation

6.8%, whereas absence of H_2 anions (41 ml) was generated. Presence of Cl^- ion had shown little enhancement in H_2 generation. Except Cl^- ions, other ions decreased H_2 generation[5]. Presence of various cations is common in industrial effluents. A reduction in photocatalytic generation of H_2 was observed in presence of $FeSO_4$ (0.5 g/l) and $CuSO_4$ (0.5 g/l) (Fig. 3), which can be attributed to negative effect on adsorption of SO_4^{2-}. Reduction in H_2 volume generated was found to be 7.3-14.6% in presence of $CuSO_4$.

Conclusions

Effect of photosensitizers and inorganic ions on solar photocatalytic generation of H_2 from H_2S was investigated. RB yielded maximum H_2 (1.3 times higher than control). Except Cl^-, other anions (I^-, NO_3^-, CO_3^{2-}, SO_4^{2}) and cations (Fe^{3+} and Cu^{2+}) retarded H_2 generation rates.

References

1 Supriya V T & Subramanyam M, Photocatalytic generation of hydrogen from hydrogen Sulfide: An energy bargain, *Int J Hydrogen Energy*, **22** (1997) 959-965.

2 Gurunathan, Maruthamuthu P & Sastri M V C, Photocatalytic hydrogen production by dye-Sensitized Pt/SnO_2 and $Pt/SnO_2/RuO_2$ in aqueous methyl viologen solution, *Int J Hydrogen Energy,* **22** (1997) 57-62.

3 Rozenkevich M B & Sakharovsky J, Photochemical behaviour of solutions of cyan-containing cobalt complexes-Efficient catalysts for Hydrogen evolution, *Int J Hydrogen Energy*, **14** (1989) 431-436.

4 Xiaojie Z, Zhiliang J, Yuexiang L, Shuben L & Gongxuan L, Visible-light-induced hydrogen production over Pt-Eosin Y catalysts with high surface area silica gel as matrix, *J Power Sources,* **166** (2007) 74-79.

5 Yuexiang L, Gongxuan L & Shuben L, Photocatalytic hydrogen generation and decomposition of oxalic acid over platinized TiO_2, *Appl Catal A: General*, **214** (2001) 179-185.