

Photoelectrochemical Hydrogen Production Using Visible Light

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Abstract- This work involves development of coaxial tubular annular photoelectrochemical reactor for hydrogen production from treatment of industrial sulfide effluent. The use of SnS as photocatalyst in a slurry reactor has been investigated. Effects of concentrations of sodium sulfide and sulfite and photocatalyst(SnS) loading on hydrogen production have been studied. For each reaction slurry there is optimum amount of catalyst loading. For instance, volume of hydrogen produced will be maximum at the catalyst loading of 0.33 g/l in reaction slurry of 0.25M sodium sulfide concentration and 0.25M sodium sulfite concentration. Further increase in the catalyst loading decreases the volume of hydrogen produced due to screening effect.

Keywords- Sodium Sulfide; Sodium Sulfite; Tin sulfide; Photocorrosion; Hydrogen; Renewable Energy.

1. Introduction

Hydrogen is the simplest, and lightest known element, is composed of one proton and one electron. More than 90% of the universe is made up of hydrogen. Sun contains more than 30% of atomic hydrogen. It is third most abundant element in the earth's surface and is found mostly in water. It is commercially used to produce ammonia for fertilizer, in solidification of oils and fats, for methanol production, in hydroalkylation, hydrocracking, hydrodesulfurisation, rocket fuel, for hydrochloric acid production, for metallic ore reduction, in cryogenics and study of superconductivity etc.

Under ordinary conditions hydrogen is colorless, odorless, tasteless, and non poisonous gas composed of diatomic molecules H_2 . Hydrogen is rich in energy, and environmental friendly when produced with solar energy. Therefore, an energy system based on solar energy, for energy generation in combination with hydrogen as an energy carrier would be environmental friendly and attractive alternative for future. Solar energy is an abundant resource and it is renewable, it is neither permanent nor constant in intensity over the world. Therefore, a suitable energy carrier for storage and transport is needed. Such an energy carrier could be hydrogen. Hydrogen is now days mainly produced by steam reforming of non-renewable natural gas. Another common process is by electrolysis of water, which is a high-energy demand process.

Considering the energy and environmental costs, neither of these processes are optimal. To meet tomorrow's demand of cheap, environmental friendly and renewable hydrogen the industries must find new ways of producing it. One solution, with high potential, is extracting hydrogen by direct water splitting in a photo-electrochemical cell. The semiconductor material should have a band gap optimized for spectral distribution of the solar radiation, for reasonable efficiency the band gap should not be much bigger than 2.0 eV[1]. Fortunately, semiconductors with band gap in the proper range usually have low resistivity against dissolution and photocorrosion, like with silicon, gallium arsenid and sulfide based semiconductors etc. Since the electrochemical potentials for hydrogen and oxygen evolution are fixed, any suitable and effective semiconductor must have also the right position of its energy edges of the conduction and valence bands. This factor limits the choice of semiconductor for water splitting.

Hydrogen bond in the organic matter and in water makes up 70% of the earth's surface. Hydrogen can be produced by breaking these bonds in water[2]. There are numerous processes to break these bonds. Theoretical decomposition potential of water at standard conditions is 1.480 V. Water electrolysis is the only process of hydrogen production, which is free of CO_2 emissions. Electrolysis separates the elements of water, hydrogen, and oxygen by charging water with an electrical current. Adding an electrolyte such as salt

improves the conductivity of water and increases the efficiency of the process [2]. Hydrogen is gathered at cathode and anode attracts oxygen. A voltage of 1.24 volts is necessary to separate hydrogen from oxygen in pure water at 25°C and 1.03 kg_f · cm⁻² pressure. Smallest amount of electricity necessary to electrolyze one mole of water is 65.3Wh (at 25°C). For producing one cubic foot of hydrogen requires 0.14 kilowatt - hours of electricity [2].

The conversion of solar energy into chemical energy has attracted considerable research efforts in recent years. The most widely investigated route is that of photochemical water splitting in sacrificial as well as cyclic photo induced system. Employing semi-conducting materials as photocatalyst. Efficient semiconducting materials for this purpose must possess certain characteristics such as suitable bandgap energies, stability towards photocorrosion, and suitable physical characteristics [3]. Nanostructured hematite ($\alpha\text{-Fe}_2\text{O}_3$) with no grain boundaries can be used for water splitting [4]. That can generate incident photon to current efficiency of about 8% by illumination through the substrate with a wavelength of 350 nm and a light intensity of 0.1 mW cm⁻² without any applied voltage [4]. The difficulty with the hematite is the charge carrier recombination due to the poor semiconductor properties in the combination with slow oxidation at the hematite nanorod/electrolyte interface. It has band gap around 2 eV. The chemical stability is good in a broad pH range. It has larger inner film area exposed to electrolyte, the size of the nano rod diameter tend to match the short hole diffusion length, facilitating the hole transport to nanostructured semiconductor / electrolyte interface. For semiconductor - based water splitting system, following criteria must be satisfied [5].

- The bandgap of the semiconductor must be greater than 1.7 eV,
- The band edges of the semiconductor must be overlapped the $\frac{H_2}{H_2O}$, and $\frac{O_2}{H_2O}$ redox potentials under $\frac{H_2}{O_2}$ evaluation conditions ,
- Charge transfer across the semiconductor - liquid interface must be fast, and
- In addition, semiconductor surface must be chemically stable in aqueous media.

Under illumination with radiation of energy greater than the semiconductor band-gap, electron-hole pairs are formed in the particle, which, in principle, can migrate to the surface. These charge carriers are able to react with suitable redox species in solution, leading to conversion of radiant to chemical energy [6]. ZnO is rather unstable in solution. ZnO works as photo anode. The presence of redox species in the solution which, in principle, can react more efficiently with the photo generated holes of the semiconductor particle will prevent the photo oxidation of the semiconductor. TiO_2 is n-type semiconductor, having band-gap 3.2eV [7]. Under illumination in the near UV region (250-400 nm), platinumized anatase TiO_2 exhibits H₂ production rates, which are

significantly higher than those of the rutile form. Photocatalytic efficiency is independent of the specific surface area of semiconductor [3]. Many semiconducting oxides have been investigated as potential photocatalysts. TiO_2 is the most suitable material, offering highest light conversion efficiency, because of its high stability towards photocorrosion and its relatively favorable bandgap energy. The rate of photocatalytic splitting of water is a strong function of the crystalline structure of TiO_2 . The rate observed over pure anatase TiO_2 is approximately 7 times higher than that over pure rutile TiO_2 . Rutile TiO_2 bandgap 3.02eV and anatase TiO_2 , bandgap 3.23eV, which favor hydrogen production over rutile TiO_2 as compared to anatase [3].

Doping of TiO_2 with cations of valency higher than that of the parent cation (Ti^{4+}) enhances the rate of hydrogen production. The photocatalytic efficiency of higher valence doped TiO_2 goes through a maximum with increasing dopant concentration in the TiO_2 matrix. Doping of TiO_2 with cations of lower valence reduces the rate of H₂ production, which decreases monotonically with increasing dopant concentration. n-type semiconductor such as CdS or ZnS are not stable in aqueous solutions, subjects to anodic photocorrosion leading to formation of sulfur and sulfite ions. ZnS has band gap 3.66eV. Zinc sulfide can only absorb the light of wavelength of 340nm or shorter [8]. ZnS oxidizes thiosulfate to sulfate, and hence produces hydrogen five times higher than CdS. It is irradiated with UV light instead of visible light due to the wider band gap of ZnS semiconductor. ZnS is unstable to light. Hence, it cannot be used for commercial hydrogen production.

Photogenerated holes may cause oxidation at the interface of n-type semiconductor, thus producing a blocking layer or dissolution of electrode, as well as solution species. This is called anodic photo corrosion. Stability of the semiconductor electrodes irradiation is thus of major concern in such cells. However, it has been reported that aqueous solutions of reducing agents acting as hole scavengers among these S^{2-} , SO_3^{2-} , or $S_2O_3^{2-}$ stabilize CdS efficiently. CdS cannot be used due to its toxicity [9].

The oxygen produced by splitting of water molecule is consumed in the oxidation of sodium sulfide [12.] leads to thiosulfate formation. Sulfide and sulfites are often present in aqueous waste streams which must be treated prior to discharge to environment. These species work as electron donors. The resultant reactions lead not only to hydrogen but also to thiosulfates which can be used as a fertilizer.

2. Limitations of Earlier Work

- Titanium dioxide has a tendency to get tarnished. Hence, it cannot be properly illuminated by light so its use for hydrogen production is ruled out. It can absorb light of wavelength below 340 nm, which is not available on earth [3].

- Cadmium sulfide has energy gap, 2.42eV[10], in the visible region but the limitation of cadmium sulfide is that it is highly toxic. Hence it cannot be used commercially due to environmental considerations [11].
- Zinc sulfide (3.66eV) produces hydrogen five times more than that obtained by using Cadmium sulfide but it cannot be used commercially because its energy gap is in the UV region [9].
- SnS, which has the bandgap of 1.2-1.4eV and absorption coefficient 104 in the visible light range [12].

Under above considerations we have to find out at acatalyst which should be non toxic and should give high rate of hydrogen production. Therefore, SnS catalyst is favorable choice that can be operated in visible region which is abundantly available on earth. Energy required to split hydrogen from water molecule is 1.24 V at 25°C and at 1 atm pressure. Hence a single photon in visible light reason is enough to produce hydrogen from water molecule. The main advantages of the photochemical excitation over the thermal route are selectivity and low reaction temperature, low operating temperatures in turn may improve selectivity, allow more favorable equilibrium conditions in exothermic reactions, and increase the feasibility of operation in liquid phase.

The rate of radiation activated is proportional to the local volumetric rate of energy absorption. This function depends on the radiation field existing in the reaction space; hence, it is required to know the radiation field within the photo reactor. The radiation energy distribution is not uniform in space due to several causes. Among them, the attenuation produced by the species absorption is always present, physical properties and geometrical characteristics of the lamp-reactor system [13].

3. Experimental Setup

It is coaxial annular reactor ($60\text{cm}(L)\times 12\text{cm}(D)$). The outer cylinder is made of steel in which a glass tube, 50 cm long, is fitted coaxially. Inside that glass tube ordinary fluorescent tube of 20 W is fitted. Within the annular space of between glass tube and steel cylinder electrolytes and catalyst are filled in slurry form. Volume required to fill the reactor is 3.5 liters. In the upper middle section hole is there to give electric connection to the tube and one hole in the annular space through which hydrogen gas comes out from the reactor to gas sampler and then gas collection jar. Line diagram of the reactor is shown in Figure 1. The slurry is recirculated with the help of pump (Industrial Engineering Works, New Delhi-15, 2880 RPM ,SR.No-0902, coupled with a motor, 925RPM). To prevent leakage in the reactor, sealant used is anabond 340®, which is the paste of Teflon (Anabond Pvt. Ltd., Chennai -600020(India)). To gas outlet, annual space tube is connected with the help of PVC tube half inch in diameter to the gas collection jar. The gas collection tube was calibrated in terms of height and volume. The water collected in 200 mm tube length was 350 ml. This means that 1 mm of tube length is equal to the 1.75 ml of water.

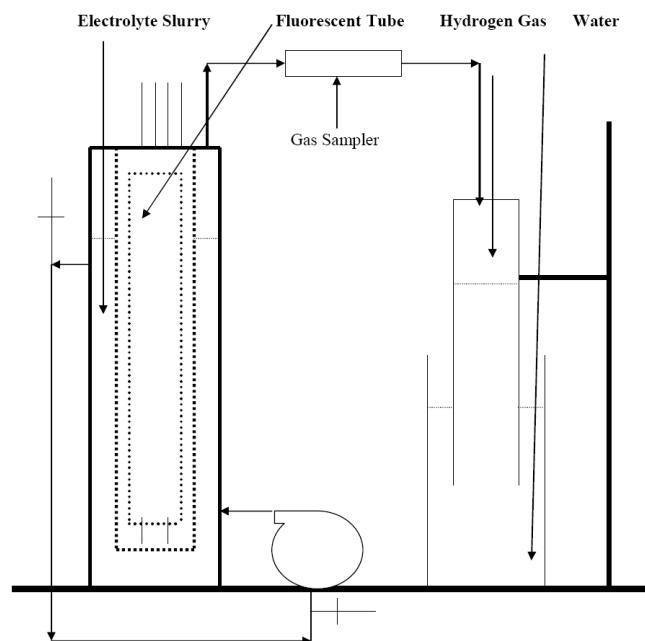


Fig. 1. Photoelectrochemical reactor for hydrogen production.

3.1. Experimentation

Sodium sulfide solution and sodium sulfite solution are prepared and mixed so as to form a 3.5 liter reaction mixture. The whole setup is to be appropriately sealed to prevent the leakage of hydrogen produced or air suction. The reaction tank is to be illuminated by an 20 W tube light. The reaction mixture is heated and recirculated by using a pump. The gas is collected by water displacement technique in collection system. Fall in water level will be the amount of the hydrogen produced. There may be some initial displacement due to some air pockets inside the reactor or pump. After experiment, reaction mixture becomes slightly greenish which indicate the sodium thiosulfate has been form in the solution. Continuous data were recorded until steady state was reached.

3.2. Catalyst Preparation

Taking calculated amount of tin chloride and tin sulfide in two beakers, each containing 500 ml distilled water. With the help of magnetic stirrer mixing is done thoroughly. After that sodium sulfide solution is poured drop by drop into the tin chloride solution with continuous stirring. The reaction occurs almost instantaneously gives a dark gray color precipitate. This precipitate is filtered and dried; finally, dark gray color crystals are formed. The precipitate separated by the filtration should be washed with distilled water before drying, to dissolve away any excess reagents and other impurities.

4. Results and Discussion

In this work, effect of electrolytes concentrations i.e. sodium sulfide concentration and sodium sulfite concentration, and photo-catalyst loading have been studied.

4.1. Effect of Electrolytes Concentration on Hydrogen Production

Effects of the two electrolytes, sodium sulfide, and sodium sulfite have been studied. Sodium sulfide absorbs the oxygen produced by splitting of water. The second electrolyte is sodium sulfite, which works as the hole scavenger. Both of the parameters are studied for different sets of conditions.

Volume of hydrogen produced increases with increase in sodium sulfide concentration initially. Trend in change in volume with concentration can be seen in the Figure 2. As we move from 0.1M to 0.2M there is a rapid change in volume. At 0.25M concentration, there is a total change in volume 24.5ml in 3 hrs, which just like the blank run. This can only be because of at experimental error that accounts to no loading of catalyst in the reaction slurry i.e. effectively zero loading. Which is justified by the repetition of this experiment thrice. The volume of the gas evolved is less than that with 0.2M concentration. As we move higher concentration volume of gas produced decreases continuously. The highest production of hydrogen is achieved at 0.2M sulfide concentration in the slurry of 0.35M Na_2SO_3 with a catalyst loading of 0.67g/l. For higher concentrations of sodium sulfide the hydrogen produced is less. The reduction of hydrogen beyond 0.3M sodium sulfide may be due to the color of solution. The light probably does not reach the photocatalyst surface.

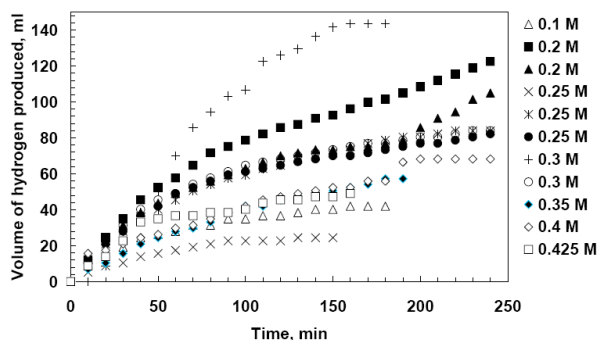


Fig. 2. Effect of sodium-sulfide concentration on hydrogen production. SnS concentration: 0.67g/l, Na_2SO_3 : 0.35M, Temperature: 60°C .

Volume of hydrogen produced with change in sodium sulfite concentration is shown in Figure 3.

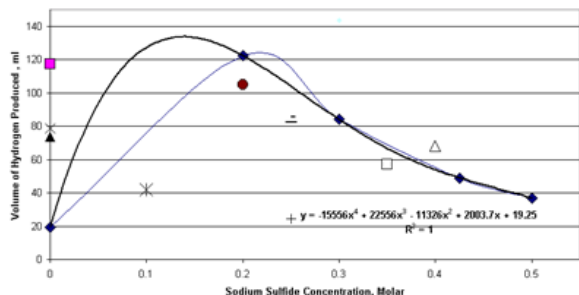


Fig. 3. Volume of hydrogen produced vs. sodium sulfite concentration. SnS loading :0.67g/l , Na_2SO_3 : 0.35M, Temperature: 60°C , Reaction time :240 min.

The sulfide used is L.R. grade and is only about 57% pure so as the sulfide concentration in the slurry increases the impurity level also increases. This leads to visible greenishness of the solution and hence reduces the photo efficiency by screening phenomena.

4.2. Effect of Sodium Sulfite Concentration on Hydrogen Production

There is nearly linear change in volume with change in sodium sulfite concentration . Changing transient hydrogen production trend can in be seen in Figure 4. At 0.1M are just like the blank run . There is a considerable amount of hydrogen produced at 0.2M concentration nearly remains same at 0.3M also. Then there is a slight decrease in the volume of hydrogen produced at 0.4M which might be within experimental error and a sharp increase for 0.5M, and 0.6M. Hydrogen produced is identical for the last two concentrations. But there is an appreciable increase in the volume of hydrogen produced as we increase the sulfite concentration 0.6M to 0.7M; nearly 3/2 times higher than that for 0.6M concentration as shown in Figure 5. The peak level of hydrogen production is reached at 0.7M sulfite concentration in the slurry of 0.35M Na_2S and the photo-catalyst loading of 0.67g/l.

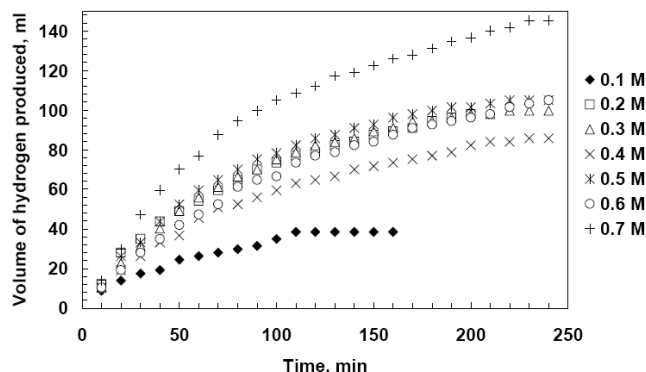


Fig. 4. Effect of sodium sulfite concentration on hydrogen production. SnS loading: 0.67g/l, Na_2S :0.35M, Temperature : 60°C .

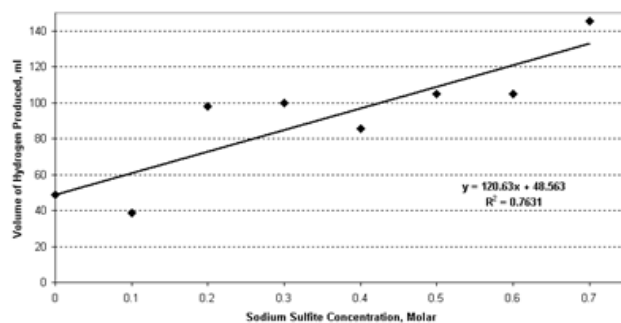


Fig. 5. Volume of hydrogen produced vs. sodium sulfite concentration. SnS loading :0.67g/l , Na_2SO_3 : 0.35M, Temperature: 60°C , Reaction time ;240 min.

4.3. Effect of Photo-Catalyst Loading on Hydrogen Production

SnS has been used as a photo-catalyst. Effect of catalyst loading has been studied only for the two sets of conditions. In the first set of conditions, sodium-sulfide concentration was zero, and sodium sulfite concentration was 0.35M. There is good amount of change in volume produced with zero catalyst loading. From this, it can be concluded that there may be some catalyst particle inside the reactor even though washing is done properly. Trend can be seen in Figure 6. At 0.67 g/l catalyst loading, we have two sets of data obtained which have nearly same values, which are 78.75 and 73.5ml. As we increase the catalyst loading, volume of hydrogen evolved increases. Volume of hydrogen production with catalyst loading can be seen in Figure 7.

In reaction slurry of 0.25M sodium sulfide concentration and 0.25M sodium sulfite concentration, there a appreciable volume of hydrogen produced at zero catalyst loading. At the catalyst loading of 0.33g/l there is a maximum in volume of hydrogen produced. Beyond this magnitude of catalyst loading; there is a decrease in volume of hydrogen produced with increasing catalyst loading. Transient hydrogen production profiles are shown in Figure 8. The screening of radiation beyond 0.33 g/l of photo-catalyst loading is the possible explanation for these observations.

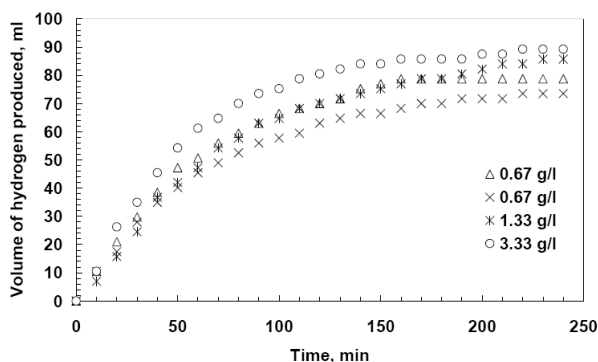


Fig. 6. Effect of catalyst loading on hydrogen production. Electrolytes: Na_2S : 0.0M, Na_2SO_3 :0.35M , Temperature: $60^\circ C$

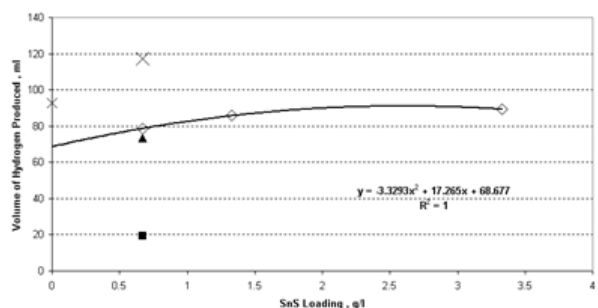


Fig. 7. Volume of hydrogen produced vs. SnS loading. Electrolytes: Na_2S :0.0M, Na_2SO_3 :0.35M, Reaction time : 240 min , Temperature : $60^\circ C$,.

Volume of hydrogen produced with change in catalyst loading can be seen in Figure 9. Absorption probability of entering photon of light and number of sites on which

adsorption and reaction will occur, will decrease with increase in the number of photo-catalyst(SnS) particles. Increased concentration of suspended particles can also have negative effects in terms of shadowing and screening phenomena that are associated with the average view factor between the particle and light source.

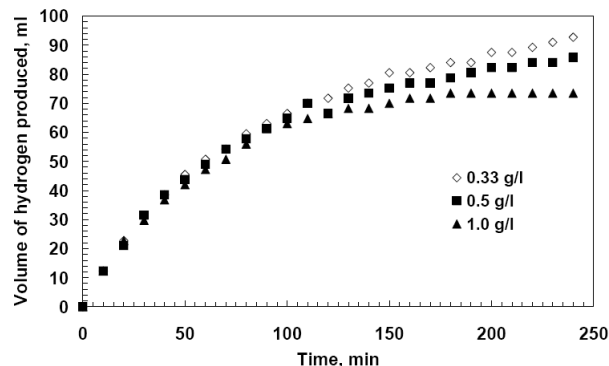


Fig. 8. Effect of photo-catalyst loading on hydrogen production. Electrolytes: Na_2S :0.25M , Na_2SO_3 :0.35M , Temperature: $60^\circ C$, Reaction time: 240 min.

At the low concentrations the rate of hydrogen production increases with increase in photo-catalyst loading, as the screening effects are negligible. At higher loadings, the screening effects increases significantly and thus the rate drops very rapidly.

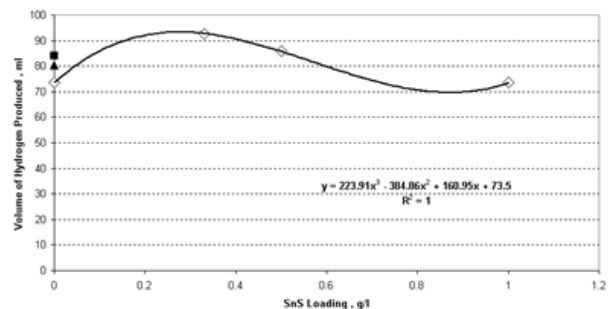


Fig. 9. Volume of hydrogen produced vs. SnS loading. Electrolytes: Na_2S :0.25M , Na_2SO_3 :0.35M , Temperature: $60^\circ C$, Reaction time : 240 min.

5. Conclusion

This can be concluded from the experiments performed that at the beginning of the reaction, the rate of hydrogen production is higher in the presence of S^{2-} ions than in a solution containing SO_3^{2-} ions. The rate of hydrogen in the solution containing S^{2-} ions is decreased due to the formation of disulfide ions, which compete with the proton reduction. The yellow disulfide acts as optical filter, reducing the light absorption.

In the presence of SO_3^{2-} ions, hydrogen generation occurs concomitantly with the oxidation of SO_3^{2-} ions to sulfate and dithionate. The rate of hydrogen evolved is a linear function of the illumination time as long as SO_3^{2-} concentration is sufficiently large.

In the solution containing both S^{2-} and SO_3^{2-} ions, formation of thiosulfate ions occurs concomitantly with hydrogen production. After the formation of thiosulfate ions, hydrogen production continues with a smaller rate due to further oxidation of thiosulfate ions to tetrathionate. The disproportionation of tetrathionate leads to formation of SO^{2-} ions that can be further oxidized to sulfate. The increasing concentration of $S_2O_3^{2-}$ ions decreases the rate of hydrogen formation attributed to their reduction by conduction band electrons.

The absorption of light by catalyst particles decreases with increase in concentration of electrolytes. In the presence of sulfide ions, hydrogen is not evolved at a constant rate because the disulfide ions resulting from the oxidation of S^{2-} ions by photoholes compete efficiency with reduction of photons.

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