



Solar Photocatalytic production of hydrogen from aqueous polystyrene-Pt/TiO₂ Suspension

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Abstract:

In the present work, the Photocatalytic production of hydrogen from aqueous suspension of polystyrene is studied using titanium dioxide doped with platinum as photocatalyst. The parameters affecting the efficiency of Photocatalytic hydrogen production are Pt-loading (%), solution pH and the Pt/TiO₂ loading and particle size. Under optimum conditions, 78 micro moles of hydrogen gas is generated after about 25 hr, irradiation in deaerated solution (pH=13, Pt weight % load is 6% and Pt/TiO₂ load and particle size are 4 gm/l and 400 mesh size respectively). Negligible amounts of hydrogen gas were noticed in the presence of unplatnized TiO₂ at pH lower than 4. The apparent quantum yield of the Photocatalytic production of hydrogen was also determined and is affected by the % load of Pt on TiO₂. The number average molecular weight of polystyrene decreases with irradiation time which indicates the photo degradation process under the condition employed. Carbon dioxide is also evolved at the later stage of photolysis process which suggests the partial mineralization of the polymer during the photolysis process. According to the experimental results a mechanism of hydrogen generation and polymer degradation is suggested.

Key words: hydrogen production; polystyrene; photocatalysis; polystyrene degradation; Pt/TiO₂ photocatalyst; TiO₂ semiconductor; solar energy conversation and storage.

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1. Introduction

Heterogeneously dispersed semiconductor surface provides both fixed environment to influence a chemical reactivity of wide range of adsorbates and mean to initiate light induced redox reactivity in these weakly associated molecules. Among semiconductor materials, n-type titanium dioxide (TiO₂ anatase) has been extensively used as a stable photocatalyst suspended in an aqueous solution. Initial interest in these photo induced redox reactions was prompted by Fujishima and Honda^[1] in 1972 discovery that water could be split to hydrogen and oxygen simultaneously upon illumination of TiO₂ with UV-Light. Since then this observation prompted extension work focused on the production of hydrogen fuel from splitting of water by means of solar energy conversion and storage.

More focused scientific interest in these chemical redox reactions also developed within the last decade, because the suggested use of photo excited semiconductor dispersion in environmental protection and amelioration^[2-4]

In the modified, typically plantinized TiO₂ semiconductor particles, the photoexcited electron production upon light illumination of the semiconductor could effectively reduce proton (H⁺) to hydrogen on the metal (Pt) surface to enhance the photocatalytic activity^[5]. Beside the platinized TiO₂ photocatalyst used for water splitting to H₂ and O₂ gases, it is also used successfully for the photo-oxidation of organic compounds such as primary alcohols, amines, or sugar...etc with the simultaneous formation of hydrogen gas (for review see reference^[6]). It was Kawai and Sakata^[7] who first in 1981 discovered that aqueous suspension of polyethylene and ploy (vinyl chloride) could be photo-oxidized to CO₂, mineral acids and hydrogen gas when irradiated with Pt/TiO₂ aqueous suspension system. Nishimoto and Coworkers^[8] have studied the possibility of H₂ gas production from the catalytic photodegradation of poly(vinyl chloride) and other vinyl polymers in alkaline and acidic solution. In the present work it is intended to utilize the visible light (xenon lamp or solar radiation) to produce hydrogen gas from polystyrene suspended particles using TiO₂ (anatase)/Pt aqueous photocatalytic system.

2. Experimental

2.1. Titanium dioxide chemicals: type anatase supplied by Fluka AG of purum grade, thermally treated at 200°C for 6 hr before being used as naked photocatalyst or used to produce Pt/TiO₂ catalyst.

2.2. Platinized TiO₂ (Pt/TiO₂): the platinized TiO₂ was produced adopting the method reported by Kracutler and Bard^[9]. By this method, the TiO₂ particles are suspended different concentrations of chloroplatinic acid and then irradiated with xenon lamp for 30 min, at room temp. to produce gray Pt/TiO₂ particles. These particles are filtered, washed with distilled water and dried under reduced pressure at 80°C. For 4 hr before being meshed in a sieve of ~400 mesh size (35 microns). By this method, 5, 10, 15, 20 and 25 weight ratio of Pt on TiO₂ particles were obtained.

2.3. Polystyrene: this polymer is prepared by the bulk polymerization of styrene monomer by free-radical polymerization using dibenzoyl peroxide as imitator at 80°C. The polymer is separated by precipitation in methanol and purified by dissolving in chloroform and reprecipitated in methanol. The polymer was grinded to a small particles (~250 mesh size). The average number molecular weigh determined viscometrically was 6x10⁵ gm/mol as calculated using Mark-Houwink equation ($[\eta]=11.2 \times 10^{-3} M^{0.73}$)^[10].

2.4. Techniques.

2.4.1. Gas chromatography: hydrogen gas analysis was carried out by gas chromatography using Pye-Unicam 404 gas chromatograph with thermal conductivity detector (TCD). Molecular sieve 5A column (5 meter/4mm) was used with nitrogen gas carrier flow rate of 30 cm/min. Column, injection and detector temperatures were 100, 80 and 125°C respectively. The volume and micromole conc. Yield of the H₂ gas is deduced by the usual calibration curve obtained by measuring the peak area of the chromatogram of H₂ gas versus the volume of the gas.

2.4.2. Photolysis apparatus: the Photolysis experiments were carried out in a photolytic Pyrex cell (capacity 35 cm³) with Pyrex window of diameter 2cm. The cell is fitted with water jacket for temp, control. A magnetic stirrer was used to keep the solution in homogenous suspension form through the Photolysis process. Nitrogen gas of purity 99.65% was used to purge the photolytic solution, bubbling rate is 50 cm³/min. The photolytic cell is located 20 cm apart from the xenon lamp (500 watt) or the concentrated solar light beam using collecting glass lenses. The light intensity measured by solar meter type 776KBE Weitres / Germany is about 150 Mw/cm² incident on the cell window.

2.4.3. Spectrophotometry: the UV-Visible spectra of polystyrene before and after different time of irradiation was measured by the double beam Hitachi/2000 Spectrophotometer. The polystyrene samples were separated by filtration and then separated from Pt/TiO₂ catalyst by dissolving in chloroform before the spectral measurements.

3. Results and discussion.

Photoirradiation ($\lambda > 300nm$) of TiO_2 / Pt suspended polystyrene aqueous solution using either xenon lamp or concentrated solar radiation lead to formation of hydrogen gas in the gas phase of the reaction cell. Figure 1 shows the dependence of hydrogen formation in micro moles in the polystyrene system on the amount of Pt loading. Negligible amount of hydrogen obtained by unplantinized TiO_2 photocatalyst. The hydrogen yield over the irradiation period 25 hr, increased drastically upon increasing platinum up to 6-8% by weight and was practically constant (plateau) over the Pt content of 8-25%. Thus a relatively small amount (6%) of Pt doping in TiO_2 semiconductor is effective for hydrogen formation in the present system. Furthermore, no hydrogen was liberated neither in the dark nor with platinum of TiO_2 alone (naked), indicating that the reaction is initiated by photoabsorption of light with wavelength $\lambda > 300nm$ [band gap of TiO_2 (anatase) is 3.2 eV] of anatase TiO_2 for electron (e^-)- hole(h^+) pairs as primary active species. Negligible amount of H_2 gas were also noticed in solution pH lower than 4. In fact, the amount of H_2 photo chemically generated is practically constant in solution pH between 4-12 and drastically increased at pH_{13} (at constant experimental conditions, e.g temp=25 , C, Pt load is 8% 140 mg/35 ml TiO_2 catalyst and 0.4gm polystyrene powder). Similar enhancement of TiO_2 /Pt photocatalytic activity in the higher pH range (pH more than 11) has been reported by Kawai and Sakata^[7] and Nishimoto and Coworkers^[8] for production of H_2 from vinyl polymers. Such pH dependence of the reaction rate is attributed to the possible modification of TiO_2 surface by strong base treatment to yield a surface (OH) group^[11]. Which is expected to become an oxidation site as shown in equation(1).

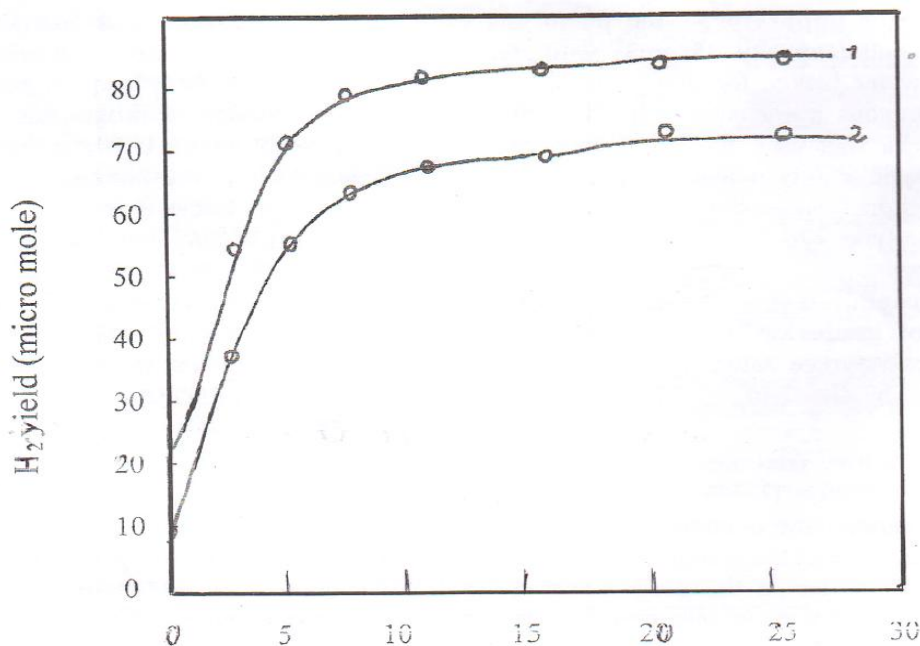
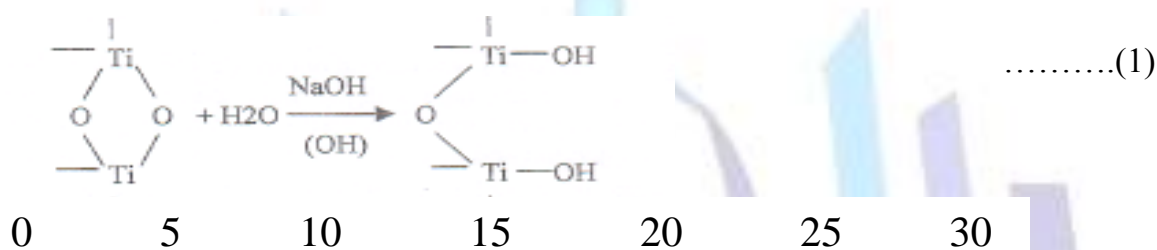


Figure1: The effect of Pt loading on the photocatalytic H_2 formation in 5M NaOH aqueous Pt/TiO_2 140 mg/35 ml suspension containing 0.4gm polystyrene. The suspension solution were irradiated for 25 hr at 25C° using: (1)500W xenon lamp. (2) Concentrated solar light [$150mW/cm^2$].

Along with H_2 gas generation, the number average molecular weight of the irradiated polystyrene is dramatically decreased. This could be explained by the main chain scission accompanying the H_2 generation which leads to a decrease in the polymer molecular weight. Table(1) shows that the number average molecular weight decreases with irradiation time under the same experimental conditions. No cross-linking or branching were detected in polystyrene after prolong irradiation in the presence of Pt/TiO_2 catalyst. However, carbon dioxide is liberated at later stages of the

photolysis experiment (after 100 hr irradiation) as detected by barium hydroxide solution. The formation of barium carbonate during the photolysis is a good indication of partial mineralization of polystyrene to carbon dioxide and water.

Table (1): The variation of the number average molecular weight of polystyrene after different time of irradiation. 0.4gm/l polystyrene in 35 ml 5M NaOH with 140mg Pt/TiO₂(Pt is 5% weight load). Reaction temp is 25C° 500W xenon lamp is used for irradiation.

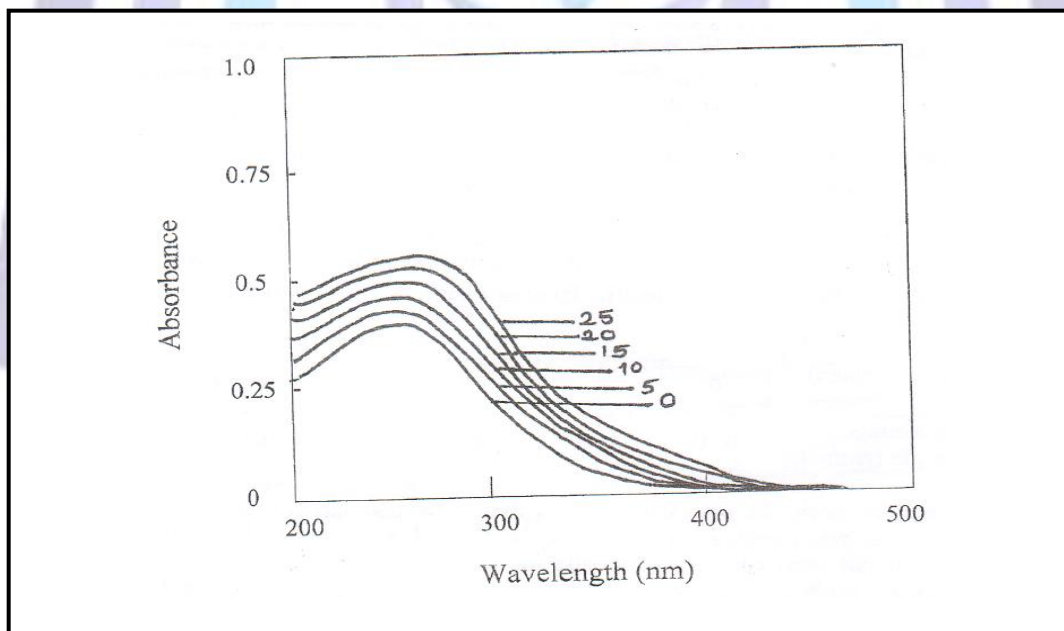
| Irradiation time (hours) | 0 | 5 | 10 | 15 | 20 | 25 |
|--|-------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Number average Molecular weight (gm/mol) | 6x10 ⁵ | 5.2x10 ⁵ | 2.1x10 ⁵ | 8.3x10 ⁴ | 6.0x10 ⁴ | 2.0x10 ⁴ |

In the present work, the apparent quantum yield of the photogeneration of H₂ gas by Pt/TiO₂ catalyst was measured according to the method suggested by Valladares and Boltn[12]. It has been considered that the incident light from xenon lamp is a quasimonochromatic beam of light centered on 365 nm and that all absorbed by Pt/TiO₂ photocatalytic system. Result of the apparent quantum yield of H₂ gas production is given in table (2) which reveals that this quantum yield steadily increases with %Pt load of TiO₂ keeping other experimental parameters constant. Therefore, the Pt loading is the important factor affecting the quantum yield. i.e the efficiency of H₂ gas production.

Table(2): The effect of present weight Pt load on the apparent quantum yield of hydrogen production from polystyrene- aqueous Pt/TiO₂ suspension in 5M NaOH. Catalyst load is 140mg/35 ml solution. Incident light intensity is 150m W/cm² using 500W xenon lamp. Reaction temp. is 25°C.

| Present weight Pt load | 0 | 2 | 5 | 10 | 15 | 20 | 25 |
|------------------------|-------|-------|-------|-------|-------|-------|-------|
| Apparent quantum yield | 0.002 | 0.008 | 0.013 | 0.033 | 0.044 | 0.056 | 0.062 |

The formation of the unsaturated double band (e.g.allyl group) or the carbonyl group through the polystyrene chain is suggested by the comparison of the UV-visible spectra of the irradiated aqueous suspension of polystyrene. The result are shown in figure(2) which show the appearance of the characteristic absorption bands between 320-240nm and grow of these bands during the photolysis process suggests the formation of carbonyl or allyl unsaturation during the photogeneration process.

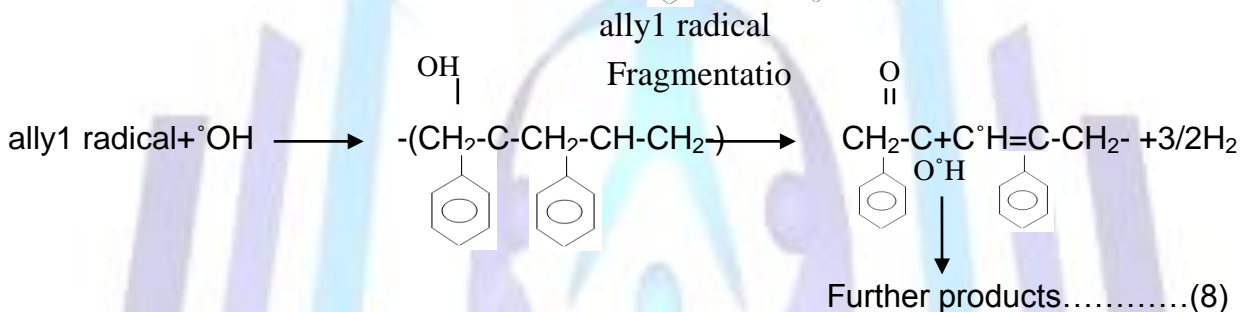
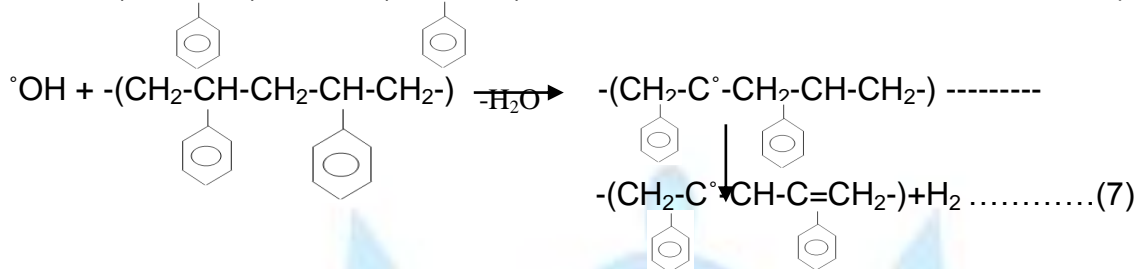


Figure(2): UV-visible spectral change of 5M NaOH aqueous solution of polystyrene suspension(0.4gm/35ml) and Pt/TiO₂ (140mg/ 5% weight Pt). Numbers on curves are the irradiation time in hours. (polystyrene spectra were recorded in chloroform solution). 500W xenon lamp is used for irradiation at 25C°.

Proposed reaction mechanism: reports in literature reveals that the photodegradation mechanism of organic or polymeric materials on TiO₂ surface is often very difficult task and a detailed pathway of the photoreaction cannot be easily be interpreted. It is well established that OH radicals is first generated (adsorbed) on TiO₂ surface due to the reaction of the adsorbed H₂O molecules with the photogenerated holes on the TiO₂ semiconductor surface.



According to the experimental results obtained we might suggest the following scheme (equations 2-8) for the catalytic photochemical reaction in this system:



The direct oxidation of polystyrene on the generated hole of TiO₂ can also occur but this is much less important than that of oxidation of H₂O to OH radical (equation 3) because the concentration and probability of adsorbed polystyrene on TiO₂ surface is much less than that of H₂O adsorption. The reaction of ·OH radicals with polystyrene and then to produce the allyl radicals and H₂ gas (equation 7) is in agreement with literature^[13]. The experimental results obtained suggest a chain scission could also occur by ·OH radicals and this brings about the decrease in molecular weight of polystyrene. The production of CO₂ is also possible on TiO₂ surface by direct mineralization of polystyrene by ·OH radical (equation 6). In conclusion, Pt/TiO₂ photocatalytic system could be successfully applied to generate H₂ gas by solar radiation of waste polystyrene suspension accompanied by simultaneous photodegradation and partial mineralization to CO₂. By this approach both plastic waste disposal as an environmental pollution problem and solar energy conversion and storage to hydrogen fuel are achieved. Alkaline solution (pH=13) and Pt load on TiO₂ surface could facilitate the generation of H₂ gas.

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