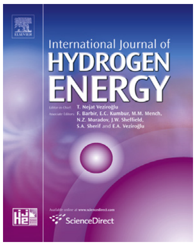
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 12718–12724



Heterogeneous photocatalytic hydrogen generation in a solar pilot plant

Katherine Villa [a], Xavier Domènech [a], Sixto Malato [b], Manuel I. Maldonado [b], José Peral [a,*]

[a] Departament de Química, Edifici Cn, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola del Vallès, Spain
[b] Plataforma Solar de Almería (CIEMAT), Carretera de Senés, km 4, 04200 Tabernas, Almería, Spain

ARTICLE INFO

Article history:
Received 28 May 2013
Received in revised form
12 July 2013
Accepted 16 July 2013
Available online 15 August 2013

Keywords:
Compound Parabolic Collector (CPC)
Hydrogen generation
Photocatalysis
Solar energy
Pilot plant

ABSTRACT

Few studies have been published about large scale heterogeneous photocatalysis hydrogen generation with simultaneous removal of organic pollutants. The purpose of the present work was to study the simultaneous photocatalytic hydrogen production and organic pollutant removal under direct solar irradiation at pilot-plant scale. The experiments were performed in a Compound Parabolic Collector (CPC) at the Plataforma Solar de Almería (PSA). The efficiencies of two different photocatalytic systems, one based on a nitrogen doped and platinized TiO_2, and the other using a platinized CdS–ZnS composite were evaluated. Formic acid and glycerol were used as sacrificial electron donors. Also, experiments using real municipal wastewaters were carried out showing simultaneous hydrogen generation and partial water pollutant removal. The largest amounts of hydrogen were obtained with aqueous solutions of formic acid, although the experiments with real wastewater gave moderate amounts of hydrogen, pointing towards the possible future use of such waters for photocatalytic hydrogen generation.

1. Introduction

Hydrogen is considered an ideal energy carrier as it can store up to 3 times as much energy as conventional natural gas and also it is environmental-friendly [1]. Although the main current way to produce it is from fossil fuels, many efforts have been directed in recent years to generate hydrogen from renewable resources [2]. In particular, there are extensive studies on the photocatalytic hydrogen production from water by using a catalyst and sunlight under ambient conditions [3–5]. The efficiency of direct water splitting process by heterogeneous photocatalysis is rather low, but it can be notably increased if the hydrogen generation is carried out in presence of aqueous sacrificial agents (electron donors) [6,7]. Moreover, an aqueous pollutant can be chosen as sacrificial agent and, thus, simultaneous hydrogen generation and pollutant removal can take place.

Among the candidate materials being examined as possible photocatalyst, titanium dioxide (TiO_2) is one of the most promising, due to its chemical stability, non-toxicity, strong oxidizing power and low-cost [8,9]. However, TiO_2 can only be excited with UV light because of its wide band gap. Therefore, to take advantage of the visible region of the solar spectrum it is necessary to promote its range of absorption into the visible. This can be achieved by doping the TiO_2 with noble metals and/or anionic species (N, S or C) [10–12]. On the

---

* *Corresponding author*. Tel.: +34 93 581 2772.
E-mail address: jose.peral@uab.cat (J. Peral).

http://dx.doi.org/10.1016/j.ijhydene.2013.07.046

other hand, CdS has also been extensively studied because it exhibits light absorption in the visible region and its conduction band edge is more negative than the H_2O/H_2 redox potential [13,14].

Few results of hydrogen generation via solar heterogeneous photocatalysis have been reported at pilot-plant scale [15–17]. Linkous et al. [16] carried out a series of experiments to guide development of reactor configurations for photochemical hydrogen production from H_2S based on semiconductor particulates. Platinized cadmium sulfide was utilized as the photocatalytic material, and powder suspensions, colloids, sedimentary dispersions and immobilized particle beds were studied at bench scale. Dengway et al. [17] designed a Compound Parabolic Concentrator (CPC) based photocatalytic hydrogen production solar reactor and they reported some preliminary results. Baniasadi et al. [15] analyzed a photo-catalytic energy conversion system for continuous production of hydrogen at a pilot-plant scale. The exergy efficiency, exergy destruction, environmental impact and sustainability index were investigated, as well as exergo environmental analyses.

Since those previous attempts were clearly preliminary, the present study aims to contribute to the area of photocatalytic hydrogen generation at large scale with solar energy. In this context, the main objective was to evaluate the optimum catalyst loading and the performance of two clearly different powdered photocatalytic systems: Pt/(TiO_2–N) (nitrogen doped and platinized TiO_2) and a Pt/(CdS–ZnS) (platinized composite of CdS and ZnS), in the H_2 production at a pilot-scale solar reactor. Also, the study focuses on the possibility of hydrogen production with real municipal wastewaters as source of electron donors. A typical stationary CPC reactor for photocatalytic water treatment was used. This type of solar collector, designed with a concentration ratio of 1 (non solar concentrated radiation), is the best option to capture both the direct and diffuse radiation. Besides, it generally exhibits high optical and quantum efficiency and low-cost [18].

2. Experimental

2.1. *Reagents*

All reagents used in this work were of analytical grade and were purchased from Sigma–Aldrich. High purity N_2 (99.9992%) was used to provide an O_2 free atmosphere. A commercial gas mixture of 1000 ppmv of H_2 in N_2 was used for GC calibration. Distilled water from PSA distillation plant (conductivity < 10 μS/cm, $SO_4^{2-} = 0.5$ mg/L, $Cl^- = 0.7–0.8$ mg/L, organic carbon < 0.5 mg/L) was used to prepare aqueous solutions. Municipal wastewater from the Sewage Treatment Plant of Almería (Spain) was used as source of electron donors.

2.2. *Photocatalyst preparation*

The photocatalysts used in this work were previously studied at laboratory scale. The Pt/(TiO_2–N) was TiO_2 Degussa P25 doped with nitrogen (NH_4NO_3 was used as source of N) and platinized. The Pt/(CdS–ZnS) was a composite of CdS and ZnS prepared by a precipitation method which was also platinized. A detailed description of the catalysts synthesis can be found elsewhere [19,20].

2.3. *Experimental setup and procedure*

The pilot plant for photocatalytic hydrogen generation consisted of a stainless steel tank of 22 L volume, fitted with gas and liquid inlet and outlet and a sampling port. Two parallel mass flow controllers could be used to control the desired N_2 gas flow into the reactor headspace during the reactor filling step. As can be seen in Fig. 1, a centrifugal pump (PanWorld NH-100PX) with a flow rate of 20 L/min was used to recirculate the aqueous slurry from the tank to the tubes of the CPC. The photoreactor was composed of 11 Pyrex glass tubes (inner diameter 28.45 mm, outer diameter 32.0 mm, length 1530.0 mm) mounted on a fixed platform tilted 37° (local latitude). The total area irradiated was 1.375 m^2 and the total volume irradiated was 9.79 L. In all experiments a total volume of 25 L was used, and the effect of catalyst loading on hydrogen production was investigated in the range of 0.2–1 g/L. Different sacrificial agents were tested: formic acid (0.05 M), glycerol (0.001 M) and a municipal wastewater (97.7 mg/L of dissolved organic carbon).

At the beginning of each experiment the aqueous slurry was recirculated in the dark for 30 min to establish the adsorption–desorption equilibrium and then the oxygen present in the gas phase volume (16 L) was pulled out with pure N_2 until no more oxygen was detected. After that, the photoreactors were uncovered and the aqueous slurry was irradiated during an average of 5 h. Gas samples were analyzed at approximately 1 h intervals. The reactor headspace remained closed during the experiment (batch conditions), although sporadic release of the pressure was done if needed.

When solar radiation is used as an energy source it is necessary to take into account two important aspects: solar radiation is not constant during the same day or during two different days (time of day, year season, meteorological conditions, etc.). Hence, in order to compare hydrogen generation data obtained in different experiments (or even at different times of the same experiment) it is necessary to normalize the data by using Eq. (1), where t_n is the experimental time for each sample, $\overline{UV}_{G,n}$ the average solar ultraviolet radiation measured by the radiometer during the period Δt_n, V_t is the total reactor volume, and A_i is the irradiated area of the reactor (CPC). $Q_{UV,n}$ (kJ/L) is the solar UV energy accumulated per reactor volume unit along the experiment, and it is used instead of the experimental time in order to normalize the hydrogen evolution. The approximate value in the system described above of $Q_{UV,n}$ on a sunny day of winter in Almería (from 8:30 h to 16:00 h) is 35–40 kJ/.

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_i}{V_t} \tag{1}$$

Solar radiation intensity was measured using a radiometer (KIPP&ZONNEN, CUV3 model) that provided data of the incident radiation corresponding to wavelengths below 400 nm and it was mounted on a platform at the same angle as the CPC. Data was recorded every minute with units of energy (W/m^2).