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ScienceDirect
Catalysis Today 124 (2007) 94–102
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Photocatalytic degradation of organic pollutants with simultaneous production of hydrogen

Alexia Patsoura, Dimitris I. Kondarides *, Xenophon E. Verykios

Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece

Available online 30 April 2007

Abstract

The photocatalytic degradation of a number of organic compounds in solution, including alcohols and organic acids, has been investigated under unaerated conditions with the use of Pt/TiO_2 photocatalyst and solar or UV irradiation. It has been found that production of CO_2 is in all cases accompanied by evolution of hydrogen, the production rate of which is significantly enhanced, compared with that obtained in the absence of organic additives in solution. Results are explained by considering that organic compounds act as sacrificial electron donors, which become progressively oxidized toward CO_2 by consuming photogenerated holes and/or oxygen. This results in decreased rates of electron–hole recombination and oxygen–hydrogen back reaction and, concomitantly, in increased H_2-production rates. The rate of photoinduced hydrogen production depends strongly on the concentration of the sacrificial agent employed and to a lesser extent on solution pH and temperature. When complete mineralization of the sacrificial agent is achieved, photogenerated oxygen can no longer be removed from the photocatalyst surface and the H_2-production rate drops to steady-state values, comparable to those obtained in the absence of the organic compound in solution. The amounts of carbon dioxide and ''additional'' hydrogen produced depend on the nature of the organic additive and are directly proportional to its initial concentration in solution. Quantification of results shows that the overall process may be described as ''photoinduced reforming of organic compounds at room temperature''. It is concluded that mineralization of organic pollutants such as alcohols and organic acids, which are common waste products of biomass processing industries, can be achieved with simultaneous production of H_2 fuel. The process may provide an efficient and cost effective method for cleaning up waste streams.

Keywords: Photocatalysis; Degradation of pollutants; Hydrogen production; Water splitting; Advanced oxidation process; Titanium dioxide; Platinum

1. Introduction

Photocatalytic processes over semiconductor surfaces have attracted significant attention in recent years as potentially efficient, environmentally friendly and low cost methods for water/air purification [1–6] as well as for renewable hydrogen production [5–10]. In both applications, photocatalytic reactions are initiated by irradiation of a semiconductor, usually TiO_2, with light energy equal to or greater than its band gap energy (E_g), which causes charge separation. The photogenerated electrons and holes may then take part in subsequent dark, redox reactions with molecules adsorbed on the photocatalyst surface to yield the final products. Degradation of organic pollutants takes place under aerated conditions with the participation of photogenerated holes, which act either directly or indirectly via generation of hydroxide radicals ($^{\bullet}OH$). Other effective oxygenating agents such as superoxide ($O_2^{\bullet -}$) or hydroperoxy ($HO_2^{\bullet}$) radicals may be also produced on the surface of TiO_2 by reduction of atmospheric oxygen [1–6,11,12]. These powerful oxidizing agents attack pollutant molecules and intermediates and ultimately lead to the production of mineralization products. It is generally accepted that practically all organic compounds can be totally oxidized into harmless compounds such as CO_2 and H_2O with the use of TiO_2 photocatalysts illuminated with UV light [1–6].

On the other hand, photoinduced production of hydrogen from water takes place under unaerated conditions and is achieved by photogenerated electrons, provided that their energy is sufficient to reduce protons toward hydrogen molecules [5–10]. In principle, direct oxygen evolution may also take place over TiO_2 photocatalysts because the oxidizing ability of photogenerated holes is sufficient to oxidize water. However,

* Corresponding author. Tel.: +30 2610 969527; fax: +30 2610 991527.
E-mail address: dimi@chemeng.upatras.gr (D.I. Kondarides).

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doi:10.1016/j.cattod.2007.03.028

production of oxygen has been rarely reported to occur over irradiated TiO_2-based photocatalysts and the possibility for achieving this at ambient conditions remains doubtful [4]. It has been proposed that photogenerated oxygen either remains adsorbed on the TiO_2 surface and/or further reacts to form peroxotitanate complexes at the surface of TiO_2 particles [13] and H_2O_2 in solution [13,14]. It is also possible that the photogenerated holes may cause oxidation of the semiconductor surface, in which case TiO_2 itself acts as an electron donor [15].

One of the major disadvantages of semiconductor photocatalytic systems, especially those involving photoinduced hydrogen production from water, is their relatively low efficiency, which is mainly limited by the recombination reaction between photogenerated electrons and holes [10]. The rate of this reaction can be retarded by deposition of noble metals on the photocatalyst surface, the role of which is to ''pump'' photogenerated electrons from the semiconductor thereby increasing the electron transfer rate to the adsorbed species and decreasing the possibility of their recombination with holes [16–18]. The recombination rate may be also suppressed substantially with the use of electron donors as sacrificial agents, the role of which is to react irreversibly with the photogenerated holes and/or oxygen thereby increasing the rate of hydrogen production [19–34]. If this sacrificial agent is an organic pollutant present in water or wastewater, the overall result would be the enhancement of the H_2 production rate with simultaneous degradation of the organic substrate.

A large variety of organic compounds have been used as electron donors for photocatalytic hydrogen production, including alcohols [23–29] and polyalcohols [29–31], sugars [31,32], organic acids [33], as well as aliphatic and aromatic compounds [20]. These compounds, especially alcohols, are satisfactory hole scavengers and undergo a relatively rapid and irreversible oxidation [10,23], which results in increased quantum yields and enhanced rates of photocatalytic hydrogen production.

In our previous work, we have investigated in detail photocatalytic cleavage of water over TiO_2-based photocatalysts [34–36] as well as degradation of azodyes in irradiated TiO_2 suspensions [37–41]. In our recent study [42], the production of hydrogen from aqueous Pt/TiO_2 suspensions illuminated with UV/vis light has been investigated in the absence and in the presence of azodyes in solution. It has been found that addition of small quantities of azodyes results in significantly enhanced rates of H_2 production for a period, which depends on dye concentration, solution pH and, to a lesser extent, solution temperature. The objective of the present study is to investigate if the same holds for other organic pollutants present in wastewaters including alcohols, organic acids, etc., which are common waste products of biomass processing industries, and to explore the possibility of combining pollutant degradation and hydrogen production into a single, efficient and cost effective process.

2. Experimental

The 0.5% Pt/TiO_2 catalyst was prepared by impregnation of titanium dioxide powder (Degussa P25) with an aqueous solution of $(NH_3)_2Pt(NO_2)_2$ (Alfa). The catalyst was characterized with respect to its specific surface area (41 m^2/g), metal dispersion (87%) and anatase-to-rutile content (75%–25%), employing nitrogen physisorption at the temperature of liquid nitrogen, selective chemisorption of H_2 at 25 °C and X-ray diffraction (XRD), respectively. Details on the equipment and procedures used for catalyst preparation and characterization can be found elsewhere [42,43].

The apparatus used for the photocatalytic experiments consists of a light source, a photoreactor and an analysis system, and has been described in detail elsewhere [42]. The lamp housing (Oriel, model 66011) is furnished with an arc lamp, a set of lenses for light collection and focusing, and a water filter, which serves for the elimination of infrared radiation. Two different light sources were used in the present study: (a) a solar light-simulating source (Xe-arc lamp, Oriel 6259, 300 W), denoted in the following as ''solar lamp'', and (b) a high pressure Xe(Hg)-arc lamp (Oriel, model 66142, 500 W), which emits in the near ultraviolet region, denoted in the following as ''UV lamp''. For the experiments reported here, the photoreactor was placed at a fixed distance from the lamp housing (50 cm) and the lamp power was kept constant at 280 W (solar source) or 450 W (UV source). Under these conditions the photon flow entering the reactor, measured by chemical actinometry [42], was found to be 1.3×10^{-6} einsteins/s or 3.5×10^{-6} einsteins/s for the solar and UV source, respectively. It should be noted that the actinometer was irradiated under conditions similar to those used for the photocatalytic experiments, thereby eliminating the need of making corrections for the reflectance and non-uniformity of the incident light beam.

The quartz photoreactor is of cubic shape and its top cover has provisions for measurements of temperature and pH and connections for inlet/outlet of the carrier gas (Ar). The gas outlet is equipped with a water-cooled condenser, which does not allow vapors to escape from the reactor. The cell is placed on a heating plate/magnetic stirrer. The analysis system consists of an on-line gas chromatograph (SRI-8610C) equipped with a molecular sieve 5A column and a TCD detector. The carrier gas is high purity Ar (99.999%). The GC is interfaced with a personal computer, which enables automatic sampling of the gas exiting from the reactor at pre-selected time intervals via an electrically actuated gas sampling valve. In selected experiments, the concentration of carbon dioxide produced by oxidation of the sacrificial agents was determined with the use of a CO_2 analyzer (Binos) connected on line at the exit of the photo-reactor.

In a typical experiment, a known amount of photocatalyst (80 mg) in powder form ($d < 90$ μm) is dispersed in triply distilled water (60 mL) under continuous stirring. When desired, the pH of the solution is adjusted with the use of NaOH or HNO_3. Sacrificial agents (Sigma Chemical Co.) are added to the solution before the addition of the photocatalyst powder and pH adjustment. After this procedure, the top cover is put in place and the cell is purged with flowing Ar to remove atmospheric oxygen from the reactor and tubing, heated to the desired temperature (40 °C, unless otherwise indicated) and

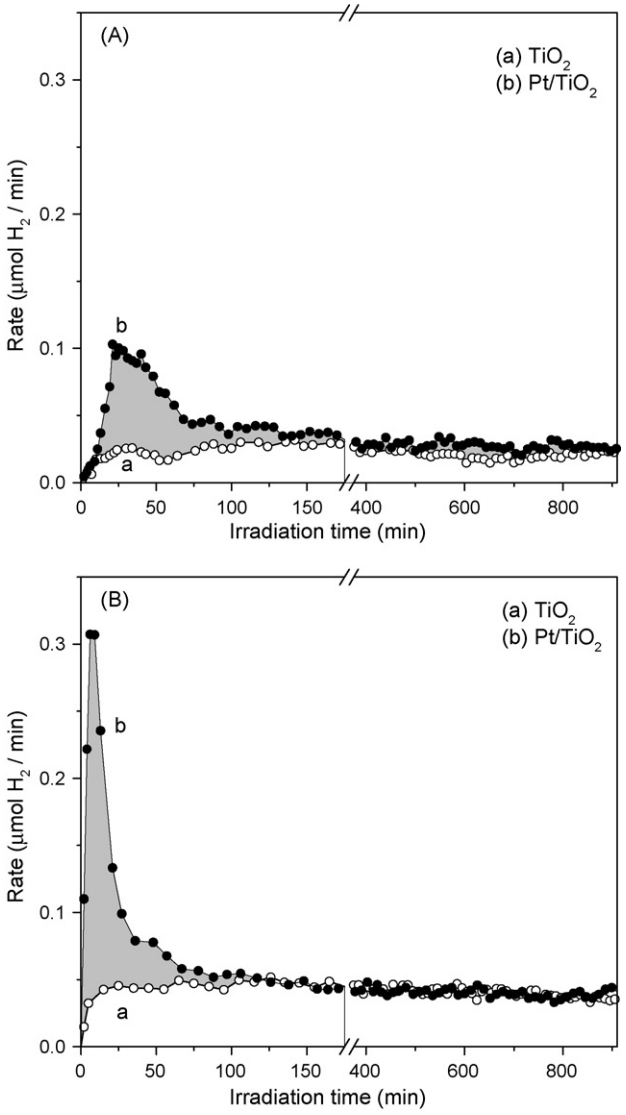

Fig. 1. Rate of hydrogen production as a function of irradiation time obtained from aqueous suspensions of TiO_2 (traces a) or 0.5% Pt/TiO_2 (traces b). Light source: (A) Xe-arc lamp (solar) and (B) Xe(Hg)-arc lamp (UV).

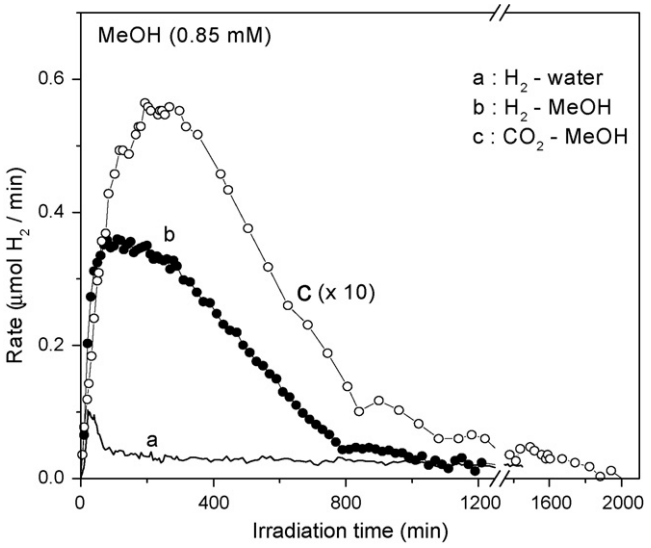

Fig. 2. Rates of hydrogen (trace b) and carbon dioxide (trace c) evolution as functions of irradiation time obtained from methanol (0.85 mM) suspensions of Pt/TiO_2. The hydrogen production curve obtained from pure water is also shown for comparison (trace a). Light source: Xe-arc lamp (solar).

then exposed to light (at $t = 0$) under continuous stirring. Experiments were conducted under an Ar flow of 20 cm^3/min, which served as means of collection and transfer of product H_2 to the analysis system. Samples were periodically collected via the automatic gas sampling valve and the concentration of H_2 present in the reactor effluent was determined by GC analysis as a function of time of irradiation.

3. Results and discussion

3.1. Effect of Pt deposition on the photocatalytic activity of TiO_2

Results obtained from aqueous photocatalyst suspensions irradiated by simulated solar light (Xe-arc lamp) are shown in Fig. 1A, where the rates of hydrogen evolution obtained with the use of bare TiO_2 (trace a) or Pt/TiO_2 (trace b) photocatalysts are plotted as functions of time of irradiation. It is observed that, in the case of unmetallized TiO_2, the rate of hydrogen production initially increases with illumination time and reaches a maximum value of 0.030 μmol/min after ca. 150 min (trace a). Prolonged exposure to light results in a small but continuous decrease of the rate, which drops to ca. 0.022 μmol/min after 900 min. Deposition of platinum (0.5 wt.%) on the photocatalyst surface results, initially, in increased H_2 production rates (trace b). In particular, the rate goes through a maximum of 0.103 μmol/min after ca. 20 min and then progressively decreases to levels comparable to those observed over the bare TiO_2 catalyst. The amount of ''additional'' hydrogen ($H_{2,add}$) produced over the platinized catalyst, with respect to that obtained from the bare semiconductor, has been calculated from the area difference between traces b and a, as schematically shown in Fig. 1A, and was found to be 4.6 μmol H_2.

Similar results obtained with the use of the UV source (Xe–Hg arc lamp) under otherwise identical experimental conditions are shown in Fig. 1B. It is observed that the responses of H_2 production rates with time are qualitatively similar to those observed under irradiation with solar light. However, both the rate maximum (0.307 μmol/min) and the pseudo steady-state rate after 900 min (0.035 μmol/min) are substantially higher in this case. The amount of ''additional'' hydrogen produced (5.8 μmol H_2) is comparable to that obtained with the use of the solar light source (4.6 μmol H_2). This indicates that $H_{2,add}$ does not practically depend on the incident photon energy or intensity (provided that $h\nu > E_g$) but only on the amount of the dispersed metal. This observation and the fact that after a certain period of illumination the platinized and unplatinized catalysts offer the same hydrogen production rate may imply that the surface of platinum is progressively ''poisoned'' during reaction. As will be discussed below, poisoning may be caused by accumulation of photogenerated oxygen.

3.2. Degradation of organic compounds with simultaneous production of H_2

The possibility of photocatalytic degradation of organic pollutants with simultaneous production of H_2 has been investigated over irradiated Pt/TiO_2 suspensions with the use of a variety of compounds, including alcohols, organic acids and aldehyde. Typical results obtained with the use of methanol (0.85 mM) are shown in Fig. 2, where the rates of H_2 (trace b) and CO_2 (trace c) evolution are plotted as functions of time of irradiation. The corresponding H_2 production curve obtained in the absence of methanol is also shown, for comparison (trace a). It is observed that the presence of methanol in the Pt/TiO_2 suspension results, initially, in significantly enhanced rates of H_2 production (trace b), compared to those obtained in the absence of the sacrificial agent (trace a). In particular, the H_2-rate goes through a maximum of 0.358 μmol/min after 80 min, which is 3.5 times higher, compared to that obtained in the absence of methanol (0.103 μmol/min). Prolonged exposure to light results in a progressive decrease of the H_2-production rate, which eventually drops to values similar to those observed in the absence of methanol in solution. The amount of ''additional'' hydrogen produced in the presence of methanol has been calculated from the area difference between trace b and trace a, and was found to be 157.4 μmol. Production of hydrogen is accompanied by evolution of CO_2 (trace c), the rate of which increases progressively with time, goes through a maximum after ca. 250 min and finally diminishes after ca. 30 h under irradiation. The total amount of CO_2 produced throughout the experiment was 36.2 μmol.

Results of Fig. 2 can be understood by considering that the role of methanol, which acts as a sacrificial agent, is to rapidly remove the photogenerated holes (hydroxyl radicals) and/or photogenerated oxygen in an irreversible fashion, thereby suppressing electron–hole recombination and/or O_2–H_2 back reaction [42]. By doing so, methanol is progressively oxidized toward CO_2, with intermediate production of formaldehyde and formic acid [26]. When complete oxidation of methanol (and reaction intermediates) is achieved, oxygen can no longer be removed from the photocatalyst surface and the rate of hydrogen production drops to steady-state values comparable to those obtained in the absence of methanol in solution. The overall process, which may be described as photo-induced reforming of methanol at room temperature, can be expressed by the following equation:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (1)$$

Considering that the amount of methanol initially added in the photoreactor was 51.0 μmol (0.85 mmol/L MeOH in 60 mL of water), stoichiometry of Eq. (1) predicts production of 153.0 μmol H_2 and 51.0 μmol CO_2, in good agreement with the experimental results of Fig. 2 (157.4 μmol H_2, 36.2 μmol CO_2, respectively).

Similar results obtained with the use of solutions of variable ethanol concentration are summarized in Fig. 3. It is observed that, in all cases, addition of ethanol results, initially, in significantly enhanced H_2 production rates (traces b), compared to those obtained in the absence of the sacrificial agent (traces a), and also to evolution of CO_2 (traces c). Increasing EtOH concentration from 0.21 mM (Fig. 3A) to 0.43 mM (Fig. 3B) and 0.86 mM (Fig. 3C) results in an increase of the rate maxima and of the total amounts of ''additional'' H_2 and CO_2 produced. In addition, the time required for the degradation of the added alcohol increases with increasing ethanol concentration, as indicated by the observation that longer irradiation periods are required to diminish CO_2 production. As in the case of methanol discussed above, the overall process may be described as reformation of ethanol at room temperature:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (2)$$

Preliminary analysis of the liquid phase with the use of HPLC showed that the reaction proceeds with intermediate formation of acetaldehyde and acetic acid, in agreement with previous studies [25]. The total amounts of ''additional'' hydrogen

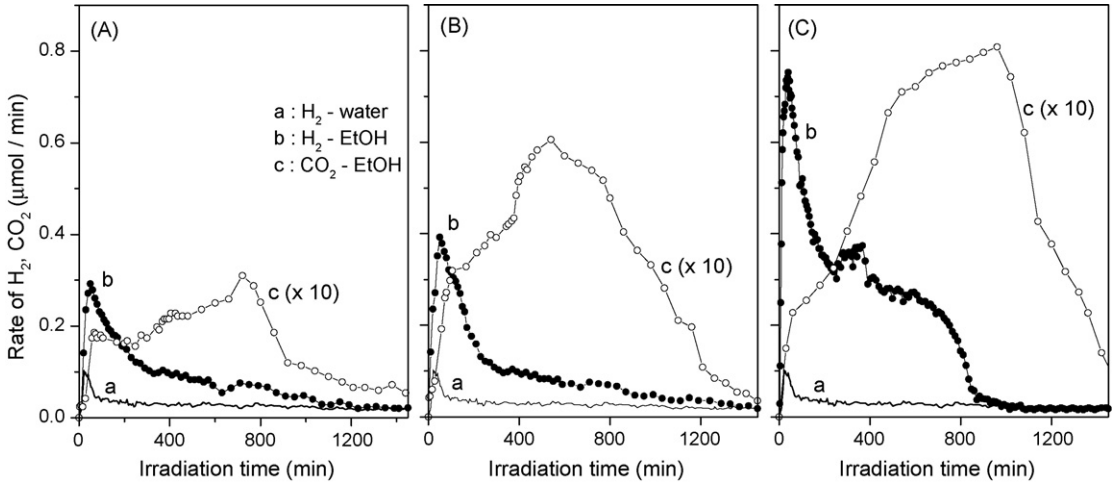

Fig. 3. Rates of hydrogen (traces b) and carbon dioxide (traces c) evolution as functions of irradiation time obtained from aqueous Pt/TiO_2 suspensions containing variable concentrations of ethanol: (A) 0.21 mM, (B) 0.43 mM, and (C) 0.86 mM. Hydrogen production curves obtained from pure water are also shown for comparison (traces a). Light source: Xe-arc lamp (solar).

(80.6 μmol) and CO_2 (24.2 μmol) produced with the use of the 0.21 mM solution (Fig. 3A) are in excellent agreement with those predicted by the stoichiometry of Eq. (2) (77.0 μmol H_2 and 25.7 μmol CO_2, respectively), providing additional evidence that ethanol acts as a sacrificial agent. As will be discussed below, the same is true for all organic compounds used in the present study.

It is of interest to note in Figs. 2 and 3 that evolution of CO_2 in the gas phase (traces c) is always delayed with respect to evolution of hydrogen (traces b). This may be due to stronger adsorption of CO_2 on the photocatalyst surface and/or due to the higher solubility of CO_2 in water and/or due to mass transfer limitations.

3.3. Effect of the nature of the organic pollutant on the rate of H_2 evolution

3.3.1. Alcohols

The effect of the nature of the added alcohol on the photocatalytic performance has been investigated with the use of aqueous solutions of methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH) or 1-butanol (ButOH), and results obtained are summarized in Fig. 4A. It is observed that, in all cases, addition of a small concentration of alcohol results in an enhancement of the rate of hydrogen production during the first hours under irradiation (traces a–d), compared to that obtained when pure water was used (trace e). It is of interest to note that for methanol and ethanol, i.e., alcohols with smaller molecular weight, production of ''additional'' hydrogen completes within 800 min (trace a) and 950 min (trace b), respectively. In contrast, the H_2 production curves for PrOH and ButOH do not fall to values corresponding to those of aqueous Pt/TiO_2 suspensions within the time period the experiment lasted, indicating that complete oxidation of these alcohols (and reaction intermediates) is more difficult to proceed under the present experimental conditions. This is probably expected, considering that for more complex molecules, oxidation will take place via formation of a larger number of reaction intermediates, i.e., more steps are required for their complete degradation. The initially higher H_2 production rates observed for methanol and ethanol (Fig. 4A) may be related to the size-dependent mobility of these compounds, which has been proposed to result in more facile hindering of recombination between photocatalytically formed oxygen and hydrogen [29].

3.3.2. Organic acids and acetaldehyde

In Fig. 4B are summarized results obtained with the use of organic acids or acetaldehyde on the rate of hydrogen evolution under solar light irradiation. It is observed that in the presence of formic acid, the rate goes through a very sharp and intense maximum of 1.70 μmol/min after only 14 min under irradiation (trace a). Interestingly, the rate diminishes after ca. 100 min and starts to increase again for prolonged exposure to irradiation, before reaching values comparable to those obtained from pure water after ca. 20 h under irradiation. When acetic acid is used, the rate maximum is significantly lower (0.39 μmol/min) and

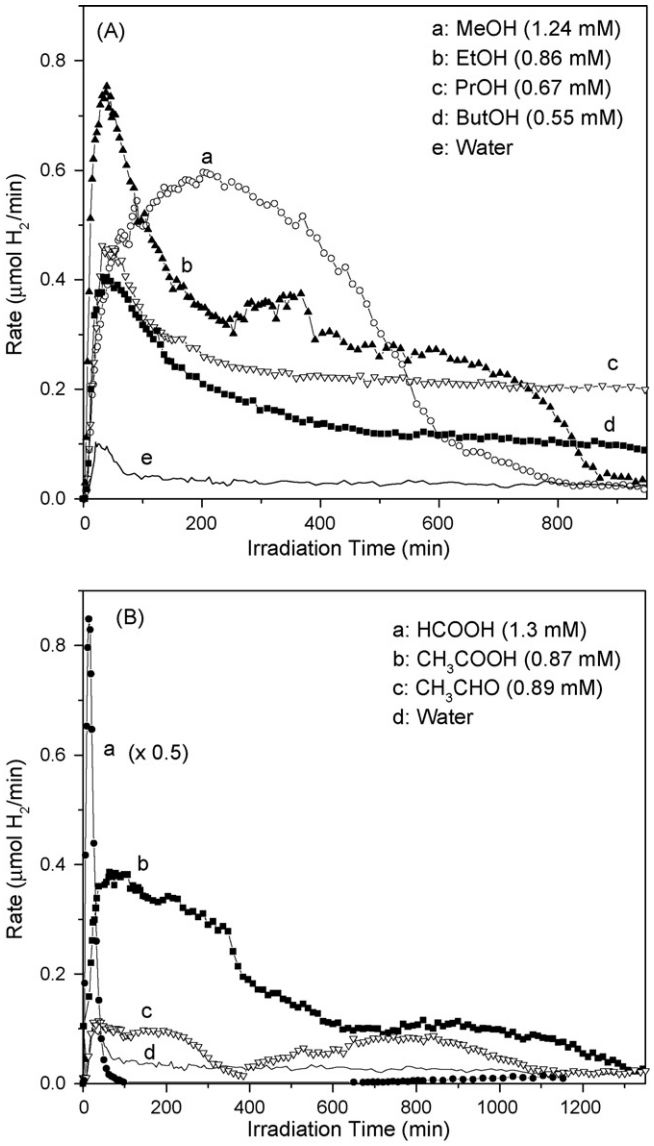

Fig. 4. Rates of hydrogen evolution as functions of irradiation time obtained from Pt/TiO_2 photocatalyst suspended in aqueous solutions of the indicated organic compounds: (A) alcohols and (B) organic acids and acetaldehyde. Light source: Xe-arc lamp (solar).

production of ''additional'' hydrogen continues for more than 20 h (trace b). The total amount of $H_{2,add}$ produced in the latter case (183.2 μmol) is in good agreement to that expected from stoichiometry of the reforming reaction of acetic acid (208.8 μmol).

Addition of acetaldehyde in the initial solution results in comparably low rates of hydrogen production (trace c). In addition, the total amount of ''additional'' hydrogen produced during the first 20 h under irradiation (72.5 μmol) is significantly lower than that expected from the stoichiometry of the reforming reaction of acetaldehyde (267.0 μmol). This indicates that photocatalytic degradation of this molecule by photogenerated oxidants is less facile, comparable to other molecules investigated. This results in lower rates of removal of photogenerated oxidants and, concomitantly, to lower hydrogen production rates.

3.4. Effects of solution pH and temperature

The effect of solution pH on the photocatalytic performance has been investigated with the use of ethanol (28.6 mM) suspensions irradiated with UV light and results are summarized in Fig. 5. It is observed that at pH 2 (Fig. 5A) the rate goes through a sharp maximum in the presence of ethanol in solution (11.5 μmol/min), at ca. 12 min under irradiation. The rate is almost two orders of magnitude higher than that obtained from pure water (0.144 μmol/min). Prolonged exposure to light results in a decrease of the rate, which, owning to the relatively large amount of ethanol initially added in solution, does not drop to values corresponding to pure water during the investigated period (20 h). Increasing solution pH to 6 (Fig. 5B) results in a substantial increase of the rate maximum, which reaches a value of 17.8 μmol/min after ca. 12 min and then progressively decreases with increasing irradiation time. Further increasing solution pH to 10 (Fig. 5C) does not result in significant changes, compared to the corresponding results obtained at pH 6.

Comparison of Fig. 5A–C shows that solution pH affects substantially the rate of H_2 production, which is favored at neutral or basic solutions. It should be noted here that the H_2-production rate in the absence of ethanol is also affected by solution pH (traces a). As has been discussed in our previous publication, this may be attributed to the increased concentrations of physisorbed OH^- groups at basic solutions, which participate in hole trapping processes and charge transfer reactions between the semiconductor and the electrolyte ([42] and references therein).

The effect of temperature on the rate of hydrogen production has been investigated in the range of 40–80 °C with the use of ethanol solutions (0.86 mM) irradiated with solar light. The H_2-production curves obtained at 60 °C and 80 °C (not shown for brevity) are qualitatively similar to those obtained at 40 °C (Fig. 4A, trace b). However, increasing temperature from 40 °C to 80 °C resulted in an increase of the rate maximum from 0.75 μmol/min (40 °C) to 0.81 μmol/min (60 °C) and 0.92 μmol/min (80 °C), which was accompanied by a progressive shift of the peaks' maximum from 40 min (40 °C) to 28 min (60 °C) and 20 min (80 °C), respectively. This behaviour, which cannot be related to light-induced reaction steps, may be rationalized in terms of (i) decreased oxygen concentration in solution with increasing temperature, (ii) more facile desorption of adsorbed species with increasing temperature, or (iii) acceleration of ''dark'', catalytic reaction steps occurring on the photocatalyst surface. Regarding the latter possibility, such a reaction step could be one between photogenerated oxygen adsorbed on the metal surface with organic molecules (ethanol or oxidized intermediates). In particular, it is possible that increasing solution temperature results in higher reaction rates between the photo-generated oxygen (or holes or other intermediate oxidants) and the sacrificial agent and, therefore, to higher rates of photo-induced hydrogen production.

3.5. Effects of sacrificial agent concentration

The effect of initial concentration of the sacrificial agent in solution on the rate of hydrogen production has been investigated with the use of aqueous Pt/TiO_2 suspensions containing variable concentrations of ethanol. Results obtained with the use of solar light irradiation are shown in Fig. 6A. It is observed that for ethanol concentrations in the range of 0.0–0.285 M (traces a–f), the H_2-production rate curves pass through maxima at 30–45 min and then progressively decrease with increasing irradiation time. It is of interest to note that the rate maximum obtained from the EtOH (1.37 M) solution (trace g) is more than 70 times higher, compared to that obtained from pure water (trace a). For the highest ethanol concentration investigated (8.91 M), the rate does not drop for prolonged exposure to light but remains at a constant value of ca. 6.6 μmol/min for about 50 h (trace h). It is only after this period that the rate starts to decrease slowly and drops to ca. 5.3 μmol/min after 65 h (results not shown for clarity). Qualitatively similar results were obtained with the use of UV light (Fig. 6B).

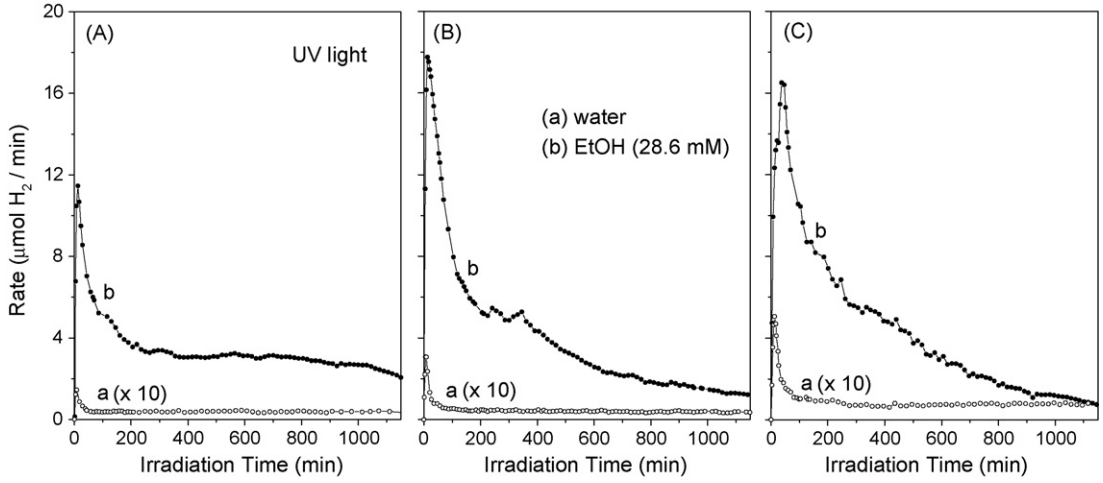

Fig. 5. Rates of hydrogen evolution as functions of irradiation time obtained from aqueous Pt/TiO_2 suspensions in the absence (traces a) and in the presence (traces b) of 28.6 mM ethanol. Solution pH: (A) 2, (B) 6, and (C) 10. Light source: Xe(Hg)-arc lamp (UV).

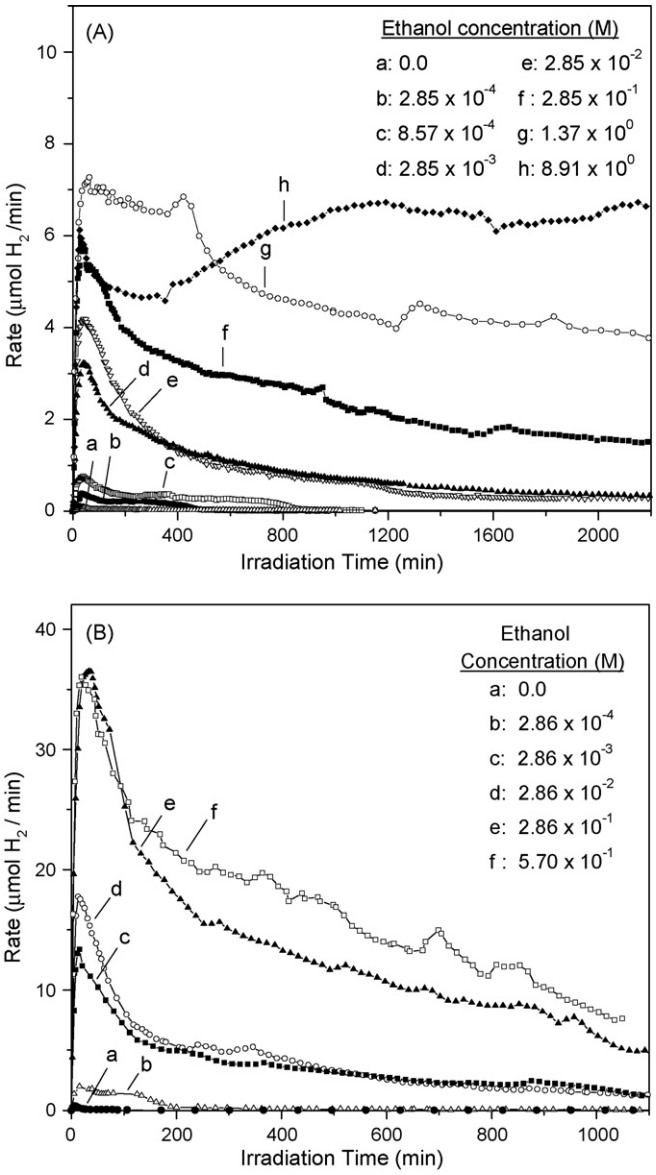

Fig. 6. Rates of hydrogen evolution as functions of irradiation time obtained from aqueous solutions of variable ethanol concentrations. Light source: (A) Xe-arc lamp (solar) and (B) Xe(Hg)-arc lamp (UV). Solution pH: natural.

Comparison with Fig. 6A shows that the H_2-production rate is significantly higher under UV irradiation. For example, the rate maximum obtained from EtOH (0.28 M) solution is about seven times higher for UV- (Fig. 6B, trace e), compared to solar-light (Fig. 6A, trace f) irradiation, and more than two orders of magnitude higher compared to that obtained from pure water (Fig. 6B, trace a).

Results presented in Fig. 6 show that increasing the concentration of the sacrificial agent results in a monotonous increase of both the rate maximum and the pseudo-steady state rate of hydrogen production. This is clearly shown in Fig. 7, where the maximum rate (r_{max}) of hydrogen production is plotted as a function of the logarithm of the sacrificial agents' concentration in solution (log C_{sacr}). It is observed that r_{max} increases linearly with increasing log C_{sacr} for the two sets of experiments investigated, for concentrations in the range of 0–

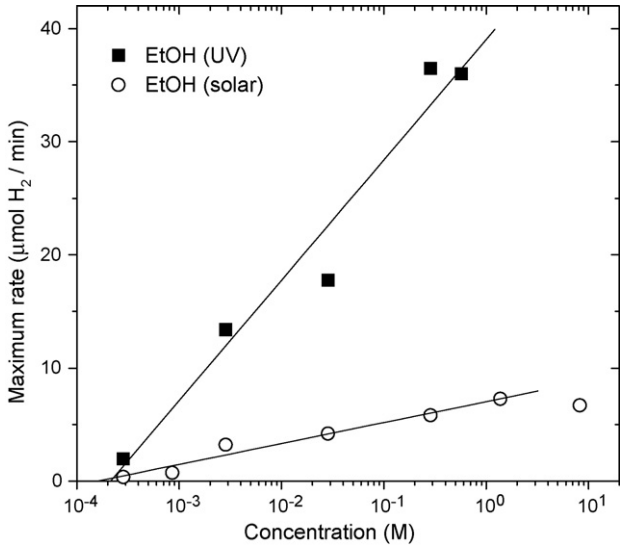

Fig. 7. Maximum rate of hydrogen evolution as a function of ethanol concentration in solution. Light source: Xe(Hg)-arc lamp (UV) or Xe-arc lamp (solar). Temperature: 40 °C; solution pH: natural (data obtained from Fig. 6).

1 M. The rate maximum is significantly enhanced under UV, compared with solar irradiation (Fig. 7).

3.6. Quantification of results and mechanistic implications

Results obtained in the absence of a sacrificial agent in solution (Fig. 1) show that, although dispersion of platinum on the TiO_2 photocatalyst surface results initially in enhanced hydrogen production rates, this beneficial effect is lost for prolonged exposure to irradiation. The fact that the amount of ''additional'' hydrogen produced under UV irradiation (5.8 μmol H_2) is comparable to that obtained with the use of the solar light source (4.6 μmol H_2) indicates that $H_{2,add}$ does not practically depend on the incident photon energy or intensity (provided that $h\nu > E_g$) but only on the amount of the dispersed metal. Preliminary experiments conducted with the use of photocatalysts of variable Pt loading (0.05–1.0 wt.%) showed that the amount of ''additional'' H_2 produced increases with increasing metal content. This provides evidence that the observed loss of the beneficial effect of Pt on the rate of H_2 production after prolonged exposure to irradiation (Fig. 1) is due to accumulation of photogenerated species on its surface, which hinder reaction steps related to the evolution of hydrogen. Since no gas-phase oxygen was detected to evolve under the present conditions, it is reasonable to suggest that species responsible for photocatalyst deactivation are oxygen-containing species, such as photogenerated oxygen strongly adsorbed on Pt [42].

When an organic compound is added in solution, the above mentioned ''deactivation'' of the Pt/TiO_2 catalyst delays in a manner which depends on the nature and amount of the sacrificial agent used (Figs. 2–4). It becomes evident that this is due to the removal of photogenerated oxygen/oxidants from the photocatalyst surface, which results in ''cleaning up'' of its surface from ''poisons'' thereby resulting in high rates of H_2 production. This is true for as long as the organic compound and

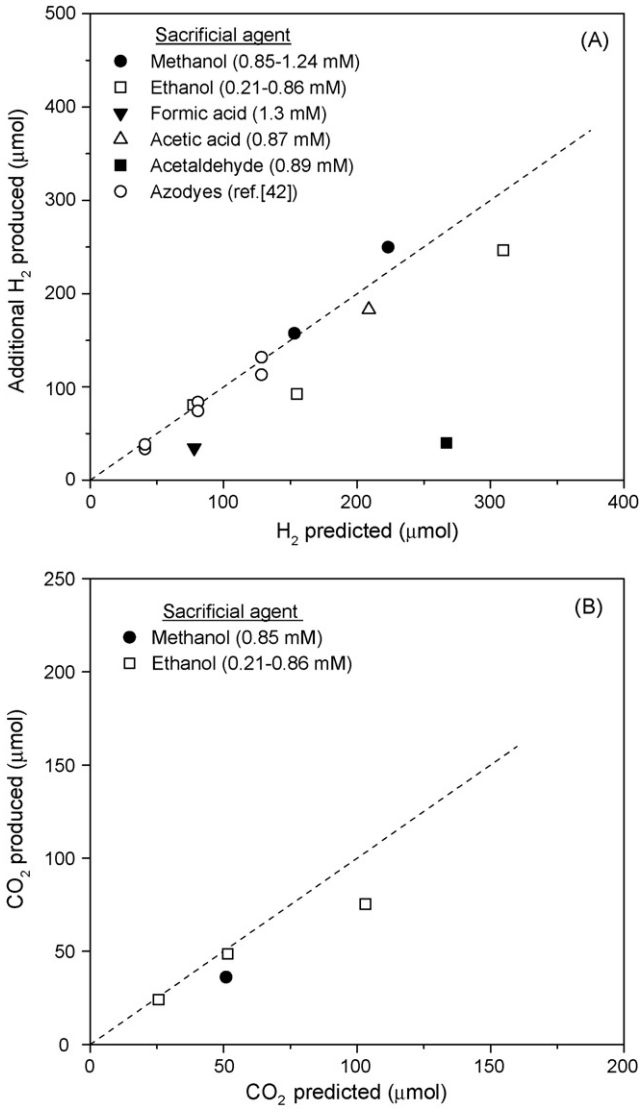

Fig. 8. Total amounts of (A) "additional" hydrogen and (B) carbon dioxide produced from irradiated Pt/TiO_2 suspensions containing the indicated sacrificial agents as functions of the corresponding amounts predicted by the stoichiometry of the reforming reaction (Eq. (3)).

intermediates are present in solution. The photocatalyst loses its activity when the sacrificial agent is totally oxidized toward CO_2.

As discussed above the overall reaction may be viewed as reforming of the organic compounds at room temperature, which can be expressed by the following general equation:

$$C_xH_yO_z + (2x - z)H_2O \xrightarrow[h\nu \geq E_g]{Pt/TiO_2} xCO_2 + (2x - z + (y/2))H_2 \quad (3)$$

The validity of this hypothesis can be tested by comparing the amounts of "additional" H_2 and CO_2 produced against those predicted by the stoichiometry of Eq. (3). This has been done for all experiments conducted with the use of small concentrations of sacrificial agents, where complete mineralization of the organic compound could be achieved during reasonable illumination times (e.g. Figs. 2–4), and results obtained are summarized in Fig. 8. It is observed that in the case of "additional" hydrogen production (Fig. 8A), the experimentally measured amounts are in very good agreement with those predicted from Eq. (3). This is true for all sacrificial agents investigated in the present study at different concentrations, and also for azodyes reported elsewhere [42]. An exception is observed for acetaldehyde, where the amount of hydrogen produced is significantly less than that predicted by the reforming reaction. The scattering of the data points around the theoretical (dotted) line may be in part due to errors introduced for the calculation of $H_{2,add}$, i.e., when subtracting H_2 curves obtained in the presence and absence of the sacrificial agent. A similarly good agreement between the measured and predicted amounts is also observed for CO_2, although not many data points are available in this case (Fig. 8B).

4. Conclusions

Results of the present study show that treatment of organic compounds present in water with the use of Pt/TiO_2 photocatalyst and solar or UV radiation under unaerated conditions results in the degradation of the pollutant with simultaneous production of gas-phase hydrogen. Organic compounds in solutions act as electron donors and scavengers of photoinduced holes and photogenerated oxygen thereby retarding electron hole recombination and hydrogen–oxygen back reaction and resulting in enhanced hydrogen production rates. The process continues for as long as the organic compound or reaction intermediates are present in solution. When complete oxidation of the sacrificial agent is achieved, the rate of hydrogen production drops to values comparable to those obtained from pure water. The amounts of hydrogen and carbon dioxide produced are directly proportional to the amount of the organic pollutant initially added in solution. The overall process may be described as photoinduced reforming of organic compounds at room temperature and represents an environmentally friendly and cost effective method for wastewater treatment, with simultaneous production of energy.

Acknowledgements

We thank the European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and, particularly the Program "PYTHAGORAS I" for funding this work.

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