pH EFFECTS ON THE ENERGETICS OF IRRADIATED TiO₂ SUSPENSIONS IN AQUEOUS D-GLUCOSE

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RéSUMÉ. — Les photocourants anodiques et les quantités d’hydrogène produits lors de l’irradiation (350 < λ < 420 nm) de suspensions aqueuses de particules de TiO₂ contenant 0,5% (en poids) de D-glucose ont été mesurés à différentes valeurs du pH. L’influence des valeurs du pH initial sur les vitesses de variation du photocourant avec le temps, ΔI/Δt, et sur les vitesses de production de l’hydrogène avec le temps ont été examinées afin d’obtenir des informations sur l’énergétique des photocatalyseurs de TiO₂ ayant des dépôts de Pt et RuO₂ à leur surface. Le transfert des électrons produits par la lumière vers les dépôts de platine et la consommation ultérieure de cette charge lors de la formation d’hydrogène dépend fortement de la concentration des protons en solution. Des solutions acides (pH 2) doivent être utilisées pour assurer le dégagement d’hydrogène dans les suspensions de TiO₂ mélangées avec des catalyseurs Pt/SiO₂, dont les dépôts de platine sont cathodiquement chargés grâce à un transfert inter-particules des électrons produits par la lumière sur les particules de TiO₂. Les dépôts de platine à la surface des particules de TiO₂ sont beaucoup plus efficaces pour collecter les électrons : des quantités plus élevées d’hydrogène ont été observées à toutes les valeurs du pH et notamment dans les milieux alcalins où l’action du D-glucose en tant que consommateur de trous est favorisé par une concentration plus élevée en ions OH⁻. Des études photoélectrochimiques et photocatalytiques conjointes sont nécessaires pour équilibrer la production des électrons (et des trous) sur les surfaces des semi-conducteurs utilisés, avec la consommation de ces charges à la surface du catalyseur.

ABSTRACT. — The anodic photocurrents and the amounts of H₂ produced under irradiation (350 < λ < 420 nm) of aqueous suspensions of TiO₂ particles containing 0.5 wt.% D-glucose were measured at various pH values. The influence of the initial pH values on the rates of change of photocurrent with time, ΔI/Δt, and on the rates of H₂ production with time was examined to obtain information on the energetics of TiO₂ photocatalysts with Pt and RuO₂ deposits. The transfer of photogenerated electrons to platinum deposits and the subsequent consumption of this charge for H₂ formation strongly depends upon the proton concentration in solution. Acidic solutions (pH 2) are necessary for H₂ evolution with TiO₂ dispersions mixed with Pt/SiO₂ catalysts, where the platinum deposits are cathodically charged through intra-particle electron transfer of the photoproduced electrons on TiO₂ particles. Platinum deposits on the TiO₂ particles themselves are much more efficient in collecting electrons; larger amounts of H₂ were produced at all pH values and especially in alkaline media where the hole scavenging action of D-glucose is also favored by a higher concentration of OH⁻ ions. A combination of photoelectrochemical and photocatalytic studies is useful in determining the balance between electron (and hole) production on illuminated surfaces of the semiconductors and consumption of these charges on the catalyst surface.

Introduction

Recently the pH dependence of the photocurrent produced at an inert electrode during the photooxidation of various polyalcohols or sugars by illuminated TiO₂ suspensions have shown that a significant increase of their hole scavenging efficiency occurs with an increase in the initial OH⁻ concentration. When the photogenerated electrons are scavenged by a pH independent redox couple such as MV²⁺ (methyl viologen) and the holes by an organic material in a reaction producing protons, the pH of the medium decreases during illumination. Under these conditions the anodic photocurrents for these aqueous mixtures decrease slowly during continuous illumination. The maintenance of an optimal pH value for a high photoactivity can be realized by the use of an appropriate catalyst capable of removing the protons produced in the anodic reaction as H₂ and to keep the initial pH constant.

The investigation of particulate TiO₂ photocatalysts by the electrochemical methods recently described, in which photogenerated electrons are collected on an inert electrode can be combined with GC measurements of the H₂ produced in the same suspensions. In this work we describe these types of experiments that were carried out to obtain more insight
about the photocatalytic properties of TiO$_2$ particles with various catalytic deposits.

D-glucose was chosen as the hole scavenger because of its efficiency$^2$ and because it is the principal component of different inexpensive biomasses that have been investigated$^6$ for the conversion of their chemical energy into H$_2$ or electricity via photocatalytic reactions. Among the recent electrochemical and photochemical investigations on the electrooxidation (on Pt electrodes)$^7$ and respectively on the photofermentation$^8$ or the photooxidation (on Pt/TiO$_2$ particles)$^6$ of D-glucose, none has described the influence of pH on these mechanisms except in some preliminary studies of polyalcohols$^{1,2}$ and sugars$^2$ in TiO$_2$ suspensions.

Experimental

**COMPONDS**

Reagent grade chemicals H$_2$PtCl$_6$ (Aldrich), RuO$_4$ (Aifa), and methyl violen chloride (Sigma Chemical Co.) were used as received. Deionized, doubly-distilled water was used to prepare all solutions.

TiO$_2$ (Degussa P25) powder having a negligible pore volume, a high anatase content and a BET area of 55 m$^2$g$^{-1}$ was used. The Pt/TiO$_2$ and Pt/SiO$_2$ catalysts were prepared as previously described$^9$ by impregnating 50 ml of stirred suspensions of 1 g TiO$_2$ (Degussa P25) or 1 g SiO$_2$ (Degussa) with the required amount of a 10$^3$% chloroplatinic acid solution. After evacuation at 350 K and drying in an oven at 400 K, the powder was flushed with N$_2$ in a Pyrex tube with the temperature increased to 573 K and then reduced in H$_2$ at 750 K for 15 hours.

RuO$_2$/TiO$_2$ catalysts were prepared by introducing the required amount of RuO$_2$ in 100 ml of a stirred suspension of 5 g TiO$_2$ followed by 2 hours heating at 325 K in a closed flask$^{12}$. Half of this suspension was loaded with platinum using the photoelectroposition technique$^{10,11}$, the calculated amount of H$_2$PtCl$_6$ was added to the RuO$_2$/TiO$_2$ suspension and irradiated with UV light for 10 minutes. The presence of Pt and Ru on the TiO$_2$ and SiO$_2$ particles was detected qualitatively by X-ray photoelectron spectroscopic and X-ray microprobe techniques. Less than 1% (by weight) quantities of Pt and RuO$_2$ were used to maintain high activity, but no attempt was made to maximize the photocatalytic activity of the particulate systems.

**APPARATUS**

Photoelectrochemical experiments were performed in a two-compartment Pyrex cell divided by a fine porosity glass frit. The larger compartment (100 ml solution volume) was equipped with a port for placement of a Beckman combination pH electrode and a flat optical window sufficiently large to allow illumination of the entire area of the TiO$_2$ suspension in the chamber. The collector electrode, a gold flag (10.6 cm$^2$), was placed in the slurry compartment near a saturated calomel electrode (SCE) used as a reference electrode. The counter electrode, a large platinum flag, was placed in the compartment separated from the slurry.

The pH of the suspension, adjusted to the desired values by addition of small amounts of either 1.0 N H$_2$SO$_4$ or 1.0 N NaOH, was measured with a Corning Model 12 pH meter. Photocurrents were recorded with a Princeton Applied Research Model 173 potentiostat/galvanostat and a Houston Instruments model 2000X-Y recorder.

The illumination source was a 3.0 kW Xe arc lamp (Christie Corp., Los Angeles, CA., Model VF30 K K) operated at 1.6 kW. In all experiments, a 10 cm water bath was used to remove IR radiation and a 350 nm cut-off filter to prevent the direct photolysis of methyl violen$^{13,14}$.

A 55 ml Pyrex flask, filled with 40 ml of suspension whose pH was initially adjusted to the desired value, was used in GC measurements of the amounts of photogenerated of H$_2$. After 1 hour of degassing with purified nitrogen, the samples, stirred at constant speed, were irradiated at 350 < $\lambda$ < 420 nm. Gas aliquots (50 to 200 µl taken from 15 ml of gas phase) were analyzed by gas chromatography (Autoprep A-700) with a 15 foot Porapak column at room temperature. No hydrocarbons (CH$_4$, C$_2$H$_6$, etc.) or CO$_2$ were observed. The main product of long term photooxidation of D-glucose on TiO$_2$ particles is a mixture of aldehydes and ketones having 6 C atoms. The chemical analysis has shown the presence of $>\text{C}=O$ and $>\text{CHO}$ functions, but the attempt to identify by GC-MS the identity of these compounds was unsuccessful.

**Results and discussion**

Illuminated suspensions of TiO$_2$ (2.5 g.l$^{-1}$) in aqueous 0.1 wt.% D-glucose at an initial pH 9 produced small anodic photocurrents (ψ ≈ 3 μA) at a gold (10.6 cm$^2$) electrode immersed in the stirred suspension. These anodic photocurrents result from the production of electron-hole ($e^- h^+$) pairs under irradiation at 350 < $\lambda$ < 420 nm and the partial consumption of holes by an electron donor like D-glucose, followed by the collection of electrons at the inert electrode$^3$. This photocurrent, always independent of the position and the orientation of the collector electrode, originates from charges on the bulk suspension. Its value decreased to essentially zero if stirring was stopped. The direct collection of electrons (exists only in instance as TiO$_2$ centers) on the particle surface by the inert electrode is rather inefficient because the rate of $e^- h^+$ recombination increases as the electrons build up on the particles. The current is low and reaches a maximum value of ψ ≈ 3 μA in less than 2 minutes.

The addition of small amounts of methyl violen dication (MV$^{2+}$), an efficient electron trapping agent$^{1,3}$ capable of reacting with the photogenerated electrons to form the reduced radical MV$^+$ that is oxidizable at the collector electrode, significantly increased the photocurrent. Under illumination, the anodic photocurrent grew to values near 1 mA, commensurate with the appearance of the blue color of MV$^+$ radical. When the light was removed, the anodic photocurrent persisted and decayed slowly to zero as MV$^+$ was oxidized at the collector electrode$^3$. Generally, stirred suspensions are rather opaque so that TiO$_2$ particles are illuminated only when they pass close to the illuminated window. The use of an efficient hole scavenger is therefore necessary to decrease the rate of $e^- h^+$ recombination and to allow the storage of the negative charge until it is trapped by an electron acceptor like methyl violen or, as discussed later, by a catalytic deposit where this charge is consumed.

The use of a same concentration of MV$^{2+}$, chosen so that [MV$^+$/MV$^{2+}$] = 1 in all experiments was necessary to maintain an excess of the electron trapping agent with respect to the electrons available on the surface of TiO$_2$ particles. The rate of photocurrent increase, ΔI/Δt, measured as initial slope on the photocurrent-time curves, was always determined for [MV$^{2+}$] = 10$^{-4}$ M, the other experimental conditions, i.e., light intensity, cell geometry, quantity of TiO$_2$ and of D-glucose, area and imposed potential of working electrode, speed of stirring, temperature, pH, were held constant unless otherwise specified.

During the continuous illumination, the pH becomes progressively lower and follows a similar time dependence (see curves 1 and 2 in Figure 1) as that of the photocurrent-time dependence simultaneously recorded. As previously reported, the consumption of the photoproduced holes, $h^+$, by alcohols$^{10,11}$, polyalcohols$^{1,2}$ or sugars$^2$ according to the suggested mechanism$^{10,11}$:

$$\text{CHOH} + h^+ \rightarrow \text{CO} + \text{H}^+ + \text{H}^+ (\text{or } H^+ + e^-)$$

(1)
depends upon the initial quantity of OH⁻ ions in the bulk. Hydrogen ions produced during the above reaction significantly decreases the initial pH value of neutral suspensions, except when H₂ was formed by using an appropriate catalyst. Effectively, the initial pH was almost constant (see curve 4 in Figure 1) when a mixture of 0.25 g TiO₂ + 0.25 g Pt (0.63 wt. %) /SiO₂ was irradiated under the same experimental conditions. Platinum deposits supported by silica can collect the negative charge produced on the TiO₂ particles (or on the existing MV⁺⁺ radicals) to reduce H⁺ ions produced during the photooxidation of D-glucose. The photocurrent observed in the presence of Pt/SiO₂ is significantly smaller (see curve 3 in Figure 1) because photogenerated electrons produce H₂ rather than being collected at the inert collector electrode. No anodic photocurrent was observed when a higher (>0.3 g) quantity of Pt (0.63 wt. %) /SiO₂ was used. Blank experiments on TiO₂ + SiO₂ mixed suspensions have shown only a slight decrease of the photocurrent compared to that for TiO₂ alone, probably because the silica particles obscure the light when they pass close to the illuminated window.

The hole scavenging efficiency of D-glucose was markedly influenced by its concentration when it was lower than 0.5 wt. % (see Fig. 2). The dependence of the Δi/Δt values with the initial pH was almost the same for suspensions containing 0.5 or 1 wt. % glucose. In all following experiments we used suspensions containing 0.5 wt. % glucose. Δi/Δt vs. pH curves were similar for 0.5 wt. % D-glucose and for 0.5 wt. % D-sorbitol. The magnitude of photocurrents and of Δi/Δt values at pH < 9 has shown that D-sorbitol, which has 6 hydroxyl groups is a more efficient hole scavenger than D-glucose, which has only 5 >CHOH groups. On the contrary, at pH > 10 the efficiency of D-glucose becomes greater than that of D-sorbitol as a result of the transformation of its aldehyde groups into two hydroxyl groups. To avoid this complication, only pH values lower than 10 were used in all following experiments.

The increase of photocurrent and Δi/Δt values when the initial concentration of OH⁻ ions increased (pH < 10) shows that hole consumption by D-glucose is favored by an increase of OH⁻ in the bulk. An obvious reason is the neutralization of H⁺ produced in reaction (1) by OH⁻.

The (0.43 wt. %) RuO₂ deposits on TiO₂ particles significantly decreased the Δi/Δt values and shifted the intercept on pH axes slightly towards more acidic values (see Fig. 3). Apparently, the presence of RuO₂ on TiO₂ surface favors electron consumption as H₂ even more than Pt/SiO₂ does. Thus, when 0.1 g of platinum loaded silica was mixed with 0.25 g of TiO₂, a decrease of Δi/Δt values was also observed, but the intercept of the Δi/Δt vs. pH plot with the pH axis was shifted towards more basic values (see curve 2 in Figure 3). The difference in the pH intercept for these two cases probably reflects the differences in the rates of the catalyzed reaction of MV⁺⁺ with H⁺ and of the reaction of holes with D-glucose.

The amount of H₂ evolved in such a mixture of TiO₂ particles with Pt loaded SiO₂ suspended in aqueous D-glucose was strongly dependent upon the initial pH value (see Fig. 4). Both the quantity of H₂ produced and the rate of its production with time of illumination show maximum values for pH 2. The inter-particle electron transfer involved in the mixed TiO₂ + Pt/SiO₂ suspensions and the catalyzed MV⁺⁺-proton reaction is favored in acidic solutions. At pH 7, H₂ evolution is low because of a low concentration of protons in the bulk solution. At high proton concentrations (e.g.,
A comparison of the \( H_2 \) production-time dependences shown in Figure 4 with \( \Delta I/\Delta t \) values in Figure 3 suggests that a lack of photocurrent at \( pH \) values more acidic than the intercepts of \( \Delta I/\Delta t \) vs. \( pH \) curves on \( pH \) axis doesn't necessarily mean that there is no photoactivity.

The electron trapping efficiency of methyl viologen strongly depends upon its concentration and on the reoxidation of MV\(^{2+} \) radicals at the collector electrode. Similarly, the electron transfer to platinum deposits depends upon the number of silica particles loaded by Pt and on the rate of \( H_2 \) evolution at these catalysts, i.e., on the quantity of \( H^+ \) in the bulk. No \( H_2 \) was observed for mixtures without D-glucose at \( pH 2 \) or for irradiation of Pt/SiO\(_2\) particles in the absence of TiO\(_2\) particles.

The presence of MV\(^{2+} \) had little influence on the amount of \( H_2 \) produced in TiO\(_2\) + Pt/TiO\(_2\) mixtures at \( pH 2 \) (compare dotted curve to curve 1 in Figure 5). The electron transfer between TiO\(_2\) particles and Pt deposits occurs directly and not through the MV\(^{2+} \) radicals. The formation of larger conglomerates between TiO\(_2\) and Pt/SiO\(_2\) particles cannot be excluded \textit{a priori}, but probably is of minor importance. Since electron transfer from the TiO\(_2\) particle cannot take place through the silica particle to reach Pt deposits, the mobility of these particles seems to be essential to accomplish successively both electron trapping and water reduction on catalyst surface.

![Figure 3](image1)

\( \Delta I/\Delta t \) vs. \( pH \) dependence for various suspensions containing 0.5 wt. of D-glucose. (1) 0.25 g TiO\(_2\) Degusa P25, (2) 0.25 g TiO\(_2\) + 0.1 g Pt (0.63 wt. %)/SiO\(_2\), (3) 0.25 g RuO\(_2\) (0.43 wt. %)/TiO\(_2\). Same cell conditions as Figure 1.

pH 1.1) the rate of \( H_2 \) production is decreased, probably because of the greatly decreased rate of hole scavenging by D-glucose, as discussed earlier.

![Figure 4](image2)

\( H_2 \) production as a function of illumination time for suspensions (40 ml) of 0.1 g TiO\(_2\) + 0.1 g Pt (0.63 wt. %)/SiO\(_2\) in aqueous glucose 0.5 wt. % containing \( 10^{-3} \ M \) MV\(^{2+} \), at various \( pH \) values.

![Figure 5](image3)

\( H_2 \) production with the illumination time for various suspensions containing \( 10^{-3} \ M \) MV\(^{2+} \) (---) or without MV\(^{2+} \) (-----). (1) 0.1 g TiO\(_2\) + 0.1 g Pt (0.63 wt. %)/SiO\(_2\), (2, 3, 4) 0.1 g RuO\(_2\) (0.43 wt. %)/TiO\(_2\) + 0.1 g Pt (0.63 wt. %)/SiO\(_2\).

![Figure 6](image4)

The presence of small (0.43 wt. %) RuO\(_2\) deposits on the surface of TiO\(_2\) particle has improved \( H_2 \) production at neutral \( pH \) values (see curves 3 and 4 in Figure 5 and compare with respective curves in Figure 4). This result is in agreement with the decrease of the photocurrent and of \( \Delta I/\Delta t \) values by RuO\(_2\) deposits and show that RuO\(_2\) is a good catalyst for \( H_2 \) formation.
The formation of $H_2$ was significantly enhanced when platinum was deposited directly on TiO$_2$ particles (compare curve 1 with dotted curve in Figure 6). Moreover, when the initial pH was increased from 2 to 10, the amount of $H_2$ was significantly increased (see Fig. 6). Clearly, photoproduced electrons are trapped more easily by Pt deposits on the TiO$_2$ surface than by those on separate SiO$_2$ particles. Even a proton concentration as low as $10^{-10}$ M was enough to allow efficient $H_2$ evolution on Pt/TiO$_2$, while no $H_2$ was observed for TiO$_2$+Pt/SiO$_2$ mixtures at pH < 7.

**Figure 6.** Comparison between the $H_2$ evolution versus illumination time for mixed suspensions (—) 0.1 g TiO$_2$ + 0.1 Pt (0.63 wt. %)/SiO$_2$ with those of loaded particles (——) 0.1 g Pt (0.63 wt. %)/TiO$_2$ curves. 1. — pH 2; 2. — pH 5.2; 3. — pH 7; 4. — pH 10, or 0.1 g Pt (0.63 wt. %)/RuO$_2$ (0.42 wt. %)/TiO$_2$, curves 5. — pH 2; 6. — pH 5.2.

A more efficient hole scavenging action of D-glucose at higher OH$^-$ concentrations explains the increasing order of curves 1, 2, 3, and 4 in Figure 6. A 0.43 wt. % RuO$_2$ deposit on TiO$_2$ particles loaded by 0.63 wt. % Pt significantly decreased the amount of the photoreduced $H_2$ at pH 3 and pH 5.2 (see curves 5 and 6 in Figure 6). This suggests a decrease of the adsorption of glucose, a decrease in the rate of photooxidation of D-glucose by the photoproduced holes, or blockage of light absorption by the RuO$_2$ deposits.

**Conclusions**

A combination of both electrochemical and gas chromatography measurements was necessary to elucidate the behavior of illuminated TiO$_2$ particles in aqueous D-glucose suspensions at different pH values. These observations are briefly summarized as follows: (1) The efficiency by which D-glucose reacts with photoproduced holes in illuminated aqueous TiO$_2$ suspensions increases with the OH$^-$ concentration. (2) $H^+$ produced during the continuous photooxidation of D-glucose can be removed by using an appropriate catalyst for $H_2$ production to maintain a constant pH value and thus a high photoactivity. (3) Significant electron transfer between the negatively charged TiO$_2$ particles after irradiation and platinum deposits on SiO$_2$ particles occurs, if the proton concentration is sufficiently high to favor the catalytic consumption of these electrons in water reduction. (4) The presence of Pt deposits on the TiO$_2$ surface greatly improves their electron trapping action and promotes $H_2$ production at alkaline pH values, where the hole scavenging action of D-glucose is favored.

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