Photocatalytic Splitting of Liquid Water by n-TiO₂ Suspension

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By illumination ($\lambda > 300$ nm) of a suspension of n-TiO₂ (grain size ≤ 0.06 μ m, 3 to 15 mg/ml) in aqueous acid solutions, containing 10^{-3} mol $\cdot$ dm⁻³ Ce⁴⁺-ions an enhanced evolution of oxygen is observed. Its yield is dependent on the amount of TiO₂ in the suspension and on the temperature. Using n-TiO₂ suspended in diluted sulfuric acid, hydrogen and oxygen were produced in a ratio of about 2:1. In both systems n-TiO₂ is acting as an efficient electron donor. For the explanation of the processes probable reaction mechanisms are proposed.

1. Introduction

The catalytic photodissociation of water can be principally achieved by various redox couples, when their redox potential, $E^\circ > 1.23$ V [1]. In an earlier work Heidt and McMillan [2—4] demonstrated the evolution of hydrogen ($Q(\text{H}_2) < 10^{-3}$) from water by illumination of aqueous acid cerous solutions with u.v.-light (254 nm; reaction 1). As a result ceric ions were formed, which produce oxygen under irradiation with light of 300—400 nm (reaction 2):

The ceric ions can be also reduced thermally ($> 30^\circ\text{C}$) [5]. Kiwi and Grätzel [6] succeeded to increase the oxygen yield by adding certain redox catalysts (PtO₂ or IrO₂). They observed for the formation of oxygen a rate of

$$k = 3 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}$$

and for the ceric ion reduction,

$$k = 1.2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}.$$

Further it was reported [7] that small amounts of H₂ and O₂ were produced by splitting of gaseous water over TiO₂ under illumination, but this effect was afterwards seriously doubted [8]. Recently, however, it was shown [9] that gas phase water can be photolysed ($\lambda > 320$ nm) to H₂ (11 μ mole per 100 mg oxydes and 20 h) and O₂ in the presence of a TiO₂/RuO₂ (8:2) mixture at room temperature. In addition it was observed [10, 11] that

platinized TiO₂ powder acts as a photocatalyst, initiating the formation of CO₂ and H₂ from gaseous water and active carbon or converting C₂H₄ and gas phase water into C₂H₆, CO₂, CH₄ and H₂. Thereby it was assumed that Pt is working as a cathode and TiO₂ as photoanode, similar to the photoelectrochemical cells. Platinized powdered TiO₂ is able to split gaseous water (~ 21 Torr) or in the presence of active carbon to promote the formation of H₂ and CO₂ [10, 11].

Recently we have reported the effect of n-TiO₂ powder, added as suspension to an aqueous acid ceric solution, on the oxygen evolution under light illumination [12]. The results of subsequent investigations on this subject are reported in this paper. It is shown that n-TiO₂ semiconductor is not only an efficient photoanode in a photoelectrochemical cell of the Fujishima-Honda-type [13, 14], but can also be applied as a photocatalyst in suspension, alone or in combination with other photoredox systems, e.g. Ce⁴⁺/Ce³⁺ for water dissociation under illumination.

2. Experimental

All chemicals (H₂SO₄, Ce(SO₄)₂ $\cdot$ 4H₂O, p.a. Merck, Darmstadt) were used without further purification. Titanium dioxide powder (98% rutil) for technical purpose was first further milled (grain size ≤ 0.06 μ m) and then heated at 1150 $^\circ\text{C}$ in a thyristor steered oven in air atmosphere for about 1 hour in order to convert it to rutil [14]. As radiation source a Hg-medium pressure lamp (HPK 125 W, Philips) was used in combination with a previously described 4 π -geometry double-wall vessel [15, 16]. It was equipped with a "Duran 50"

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filter, cutting off light with $\lambda < 300$ nm. The solutions (about 150 ml) were prepared using at least four times distilled water and were purged with high purity argon (Messer Griesheim, Vienna) for about 1 hour in order to remove oxygen. During irradiation the temperature was kept constant by means of a thermostat. The absorption spectra were measured with a spectrophotometer "Coleman 565" (Perkin Elmer). The evolved gas was collected by a vacuum line and analysed by gaschromatography.

3. Results and Discussion

For convenience both systems, $\text{Ce}^{4+}/\text{Ce}^{3+}\text{-TiO}_2$ and $\text{H}_2\text{SO}_4/\text{TiO}_2$, will be treated separately.

3.1. The $\text{Ce}^{4+}/\text{Ce}^{3+}\text{-TiO}_2$ System

The previously observed effect on the photosensitized O_2 -formation in an aqueous acid ($0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$) $\text{Ce}^{4+}/\text{Ce}^{3+}$ solution in the presence of n-TiO_2 suspension [12], was now further investigated. The acid aqueous suspension consisting of Ce^{4+} ions ($\lambda_{\text{max}} = 320$ nm, $\epsilon_{320} = 4.7 \times 10^2 \text{ m}^2 \cdot \text{mol}^{-1}$) and TiO_2 ($\lambda_{\text{max}} \sim 355$ nm) was illuminated under intensive stirring at 30°C and the evolved gases were pumped out and analysed. Some experiments were performed also at 10 and 60°C under otherwise equal conditions.

By irradiating of airfree solutions of $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ Ce}^{4+}$ and $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ for 15 min at 30°C in the absence of n-TiO_2 the observed oxygen yield did not exceed $0.2 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$. However, by adding n-TiO_2 powder to the solution under the same experimental conditions the O_2 evolution rose rapidly, as can be seen in Figure 1. A maximum yield of about $8 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$ was obtained in the presence of 10 mg $\text{n-TiO}_2/\text{ml}$ solution of $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ Ce}^{4+}$ and $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$. The decrease of the yield is probably due to the insufficient stirring under the experimental conditions and by the limited Ce^{4+} concentration applied.

The O_2 formation was also studied as a function of irradiation time using 3 mg $\text{n-TiO}_2/\text{ml}$ solution, and the results are presented in Figure 2.

The obtained curve shows first a strong increase from $1.8 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$ at 5 min to above $6 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$ about 50 min irradiation time and a steep decrease above 60 min. Following the concentration change of Ce^{4+} in the solution at the same time spectrophotometrically it was found that the photoproduction of oxygen is proportional

Fig. 1. Dependence of O_2 -evolution from n-TiO_2 amount in the suspension (Solution: $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ Ce}^{4+}$, $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$, 15 min irradiation time at 30°C).

Fig. 2. Formation of O_2 as a function of illumination time. (Solution: $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ Ce}^{4+}$, $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$; 3 mg n-TiO_2 powder/ml, 30°C).

to the Ce^{4+} consumption. This effect is demonstrated in Figure 3.

The observed formation of small amounts of oxygen in the absence of TiO_2 powder in the Ce^{4+} solution is based on the known reaction (2).

In order to explain the role of the n-TiO_2 in the strongly enhanced photoproduction of oxygen from liquid water it is to be considered that part of the light ($\lambda > 360$ nm) is mostly absorbed by the semiconductor. As a result, each absorbed quantum promotes an electron from the valence band to the conductivity band (energy gap, $\Delta E \cong 3.1 \text{ eV}$, $\lambda \leq 400 \text{ nm}$):

Fig. 3. O₂-formation as a function of Ce⁴⁺-consumption (System: 10⁻³ mol · dm⁻³ Ce⁴⁺, 0.5 mol · dm⁻³ H₂SO₄; 3 mg n-TiO₂ powder/ml, at 30 °C). (a) O₂ at 10 °C, (b) at 30 °C and (c) at 60 °C, experimental conditions as above.

The transients (TiO₂⁺ · e⁻) on the particle surface can act as electron donor, reducing the Ce⁴⁺ ions under formation of positively charged centres (so called p⁺ holes, TiO₂⁺), which can split the water, reforming n-TiO₂:

Thereby two individual reaction steps are assumed:

a) Reaction of water molecules with positively charged holes (p⁺) on the surface of each individual n-TiO₂ particle, where H₂O⁺ transients are formed. The last ones are known to be very reactive toward water molecules, leading to the formation of OH-radicals [17].

b) The OH-radicals are oxidized on the particle surface in a second reaction step, namely:

From the brutto equations (4) and (5) is obvious that the O₂ formation is dependent on the Ce⁴⁺ concentration (Figure 3). As mentioned above reaction (2) is temperature dependent. The role of this effect was studied by performing additional three series of experiments at 10, 30 and 60 °C (solution: 10⁻³ mol · dm⁻³ Ce⁴⁺, 0.5 mol · dm⁻³ H₂SO₄, 3 mg/ml n-TiO₂ powder, 45 min irradiation time). The mean O₂-yields are presented as (a) at 10 °C, (b) at 30 °C and (c) at 60 °C in Figure 3. It is obvious that with

an increase of the temperature to 60 °C an enhanced O₂-yield is obtained (7 × 10⁻⁵ mol · dm⁻³ O₂), but about 90% Ce⁴⁺ is consumed. At 10 °C, however only about 50% Ce⁴⁺ is used up to produce 6 × 10⁻⁵ mol · dm⁻³ O₂, whereas the result at 30 °C lies on the line as expected. These facts indicate that at higher temperatures two processes are involved: photocatalytical and thermochemical. At low temperatures the catalytical process involving TiO₂ (reaction 4 to 9) is predominant.

The reaction mechanism is still not elucidated and further experiments are in progress.

3.2. The H₂SO₄/n-TiO₂ System

Considering the above discussed effect of n-TiO₂ suspension on the photochemical water oxidation a similar behaviour with other systems can be expected. As a further model for this purpose airfree solutions of aqueous sulfuric acid (10⁻³ to 1 mol · dm⁻³ H₂SO₄) in the presence of 5 mg/ml n-TiO₂ powder were irradiated. In this case the light (λ > 300 nm) was practically absorbed by TiO₂ only, since the diluted sulfuric acid absorbs below 300 nm, whereby ε₃₀₀(H₂SO₄) = 0.007. The experimental conditions were the same as described above. During the irradiation (45 min at 30 °C) the suspension was intensively stirred. The evolved gas mixture was collected by a vacuum line and analyzed by gaschromatography.

The aqueous H₂SO₄/TiO₂ system delivered under illumination hydrogen and oxygen, the yields of which increased with the concentration of sulfuric acid as shown in Figure 4.

Fig. 4. H₂ and O₂ yields as a function of sulfuric acid concentration (Solution: 10⁻³ to 1 mol · dm⁻³ H₂SO₄, 5 mg/ml n-TiO₂; irradiation: 45 min at 30 °C).

It is of interest to note that the ratio of the H₂/O₂ yields is about 2. Based on this a consistent reaction mechanism is proposed. It is assumed that the (TiO₂⁺ · e⁻) species is acting as a very efficient electron donor for the H_{aq}⁺, producing H-atoms, which combine to hydrogen molecules. Thereby the surface of the n-TiO₂ particles serves as an electron pool, where neutralization reactions take place.

$$(k_{12} = 1.15 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad [18].$$

$$(k_{13} = 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad [19].$$

By reaction (10) a very active n-TiO₂⁺ surface is formed, which initiates O₂ production according to reactions (5) to (9). Reaction (12) can play a role for the H-atoms diffused far away from the particle surface. Finally it is to be noted that two light quanta are needed for the splitting of 1 molecule H₂O to hydrogen and oxygen.

It is to be mentioned that, using 0.5 mol · dm⁻³ H₂SO₄ without addition of n-TiO₂ powder, very low yields for hydrogen (~ 0.3 × 10⁻⁶ mol · dm⁻³ H₂) and oxygen (~ 0.2 × 10⁻⁶ mol · dm⁻³ O₂) were obtained. This is due to the direct photolysis of the sulfuric acid, since [20]:

$$(k_{15} = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad [21]$$

Persulfuric acid is relatively by unstable and under illumination leads to O₂ formation and a mixture of sulforous and sulfuric acids. This process (reactions 13 to 15) can be suppressed by using light with λ > 350 nm.

4. Conclusions

Experimental evidence is presented for the ability of illuminated (λ > 300 nm) n-TiO₂ suspension to act as a very efficient electron donor, which is regenerable under proper experimental conditions. A photoinduced oxidation of water is observed, when Ce⁴⁺ ions serve as electron acceptor in the presence of n-TiO₂. The O₂ yield is dependent upon temperature and the amount of added semiconductor. Using H_{aq}⁺ as electron acceptor and n-TiO₂ as electron donor the water is split to H₂ and O₂ under the influence of light.

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