Photocatalytic Splitting of Liquid Water by n-TiO_2 Suspension

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By illumination ($\lambda > 300$ nm) of a suspension of n-TiO_2 (grain size $\leqq 0.06$ mm, 3 to 15 mg/ml) in aqueous acid solutions, containing 10^{-3} mol · dm^{-3} Ce^{4+}-ions an enhanced evolution of oxygen is observed. Its yield is dependent on the amount of TiO_2 in the suspension and on the temperature. Using n-TiO_2 suspended in diluted sulfuric acid, hydrogen and oxygen were produced in a ratio of about 2 : 1. In both systems n-TiO_2 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 ($Q(H_2) < 10^{-3}$) 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):

$$Ce^{3+} + H_2O \rightsquigarrow Ce^{4+} + OH^- + 1/2\,H_2\,, \quad (1)$$

$$4\,Ce^{4+} + 2\,H_2O \rightsquigarrow 4\,Ce^{3+} + 4\,H^+ + O_2\,. \quad (2)$$

The ceric ions can be also reduced thermally ($>30\,°C$) [5]. Kiwi and Grätzel [6] succeeded to increase the oxygen yield by adding certain redox catalysts (PtO_2 or IrO_2). They observed for the formation of oxygen a rate of

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

and for the ceric ion reduction,

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

Further it was reported [7] that small amounts of H_2 and O_2 were produced by splitting of gaseous water over TiO_2 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 H_2 (11 μmole per 100 mg oxydes and 20 h) and O_2 in the presence of a TiO_2/RuO_2 (8:2) mixture at room temperature. In addition it was observed [10, 11] that platinized TiO_2 powder acts as a photocatalyst, initiating the formation of CO_2 and H_2 from gaseous water and active carbon or converting C_2H_4 and gas phase water into C_2H_6, CO_2, CH_4 and H_2. Thereby it was assumed that Pt is working as a cathode and TiO_2 as photoanaode, similar to the photoelectrochemical cells. Platinized powdered TiO_2 is able to split gaseous water (~ 21 Torr) or in the presence of active carbon to promote the formation of H_2 and CO_2 [10, 11].

Recently we have reported the effect of n-TiO_2 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-TiO_2 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. Ce^{4+}/Ce^{3+} for water dissociation under illumination.

2. Experimental

All chemicals (H_2SO_4, $Ce(SO_4)_2 \cdot 4\,H_2O$, p.a. Merck, Darmstadt) were used without further purification. Titanium dioxide powder (98% rutil) for technical purpose was first further milled (grain size $\leqq 0.06$ mm) and then heated at 1150 °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 4π-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 spectralphotometer "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, Ce^{4+}/Ce^{3+}-TiO_2 and H_2SO_4/TiO_2, will be treated separately.

3.1. The Ce^{4+}/Ce^{3+}-TiO_2 System

The previously observed effect on the photosensitized O_2-formation in an aqueous acid (0.5 mol · dm^{-3} H_2SO_4) Ce^{4+}/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 ($\lambda_{max} = 320$ nm, $\varepsilon_{320} = 4.7 \times 10^2$ m^2 · mol^{-1}) and TiO_2 ($\lambda_{max} \sim 355$ 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} mol · dm^{-3} Ce^{4+} and 0.5 mol · dm^{-3} H_2SO_4 for 15 min at 30 °C in the absence of n-TiO_2 the observed oxygen yield did not exceed 0.2×10^{-5} mol · dm^{-3} 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 8×10^{-5} mol · dm^{-3} O_2 was obtained in the presence of 10 mg n-TiO_2/ml solution of 10^{-3} mol · dm^{-3} Ce^{4+} and 0.5 mol · dm^{-3} H_2SO_4. The decrease of the yield is probably due to the unsufficient stirring unter 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 n-TiO_2/ml solution, and the results are presented in Figure 2.

The obtained curve shows first a strong increase from 1.8×10^{-5} mol · dm^{-3} O_2 at 5 min to above 6×10^{-5} mol · dm^{-3} 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

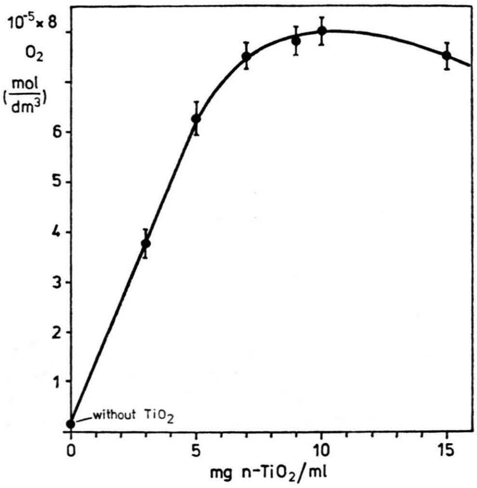

Fig. 1. Dependence of O_2-evolution from n-TiO_2 amount in the suspension (Solution: 10^{-3} mol · dm^{-3} Ce^{4+}, 0.5 mol · dm^{-3} H_2SO_4, 15 min irradiation time at 30 °C).

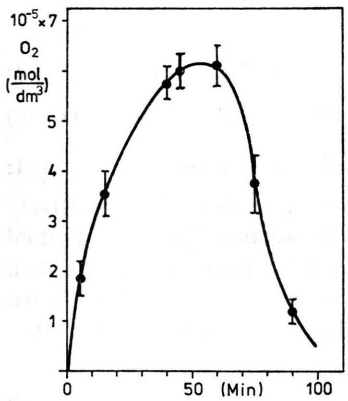

Fig. 2. Formation of O_2 as a function of illumination time. (Solution: 10^{-3} mol · dm^{-3} Ce^{4+}, 0.5 mol · dm^{-3} H_2SO_4; 3 mg n-TiO_2 powder/ml, 30 °C).

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, $\Delta E \simeq 3.1$ eV, $\lambda \leq 400$ nm):

$$TiO_2 \rightsquigarrow {}^*TiO_2 \rightarrow (TiO_2^+ \cdot e^-) . \quad (3)$$

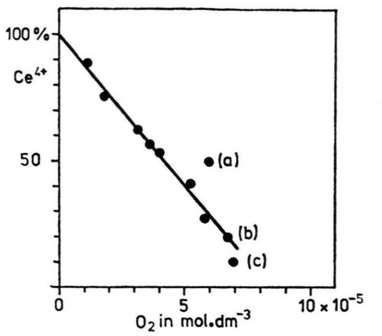

Fig. 3. O_2-formation as a function of Ce^{4+}-consumption (System: 10^{-3} mol · dm^{-3} Ce^{4+}, 0.5 mol · dm^{-3} H_2SO_4; 3 mg n-TiO_2 powder/ml, at 30 °C). (a) O_2 at 10 °C, (b) at 30 °C and (c) at 60 °C, experimental conditions as above.

The transients ($TiO_2^+ \cdot e^-$) on the particle surface can act as electron donor, reducing the Ce^{4+} ions under formation of positively charged centres (so called p^+ holes, TiO_2^+), which can split the water, reforming n-TiO_2:

$$(TiO_2^+ \cdot e^-) + Ce^{4+} \rightarrow TiO_2^+ + Ce^{3+}, \quad (4)$$

$$4\,TiO_2^+ + 2\,H_2O \rightarrow 4\,TiO_2 + 4\,H^+ + O_2. \quad (5)$$

Thereby two individual reaction steps are assumed:

a) Reaction of water molecules with positively charged holes (p^+) on the surface of each individual n-TiO_2 particle, where H_2O^+ transients are formed. The last ones are known to be very reactive toward water molecules, leading to the formation of OH-radicals [17].

$$H_2O + TiO_2^+ \rightarrow TiO_2 + H_2O^+, \quad (6)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH. \quad (7)$$

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

$$OH + TiO_2^+ \rightarrow TiO_2 + H^+ + O, \quad (8)$$

$$2O \rightarrow O_2 \quad \text{(very fast)}. \quad (9)$$

From the brutto equations (4) and (5) is obvious that the O_2 formation is dependent on the Ce^{4+} 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} Ce^{4+}, 0.5 mol·dm^{-3} H_2SO_4, 3 mg/ml n-TiO_2 powder, 45 min irradiation time). The mean O_2-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 O_2-yield is obtained (7×10^{-5} mol · dm^{-3} O_2), but about 90% Ce^{4+} is consumed. At 10 °C, however only about 50% Ce^{4+} is used up to produce 6×10^{-5} mol · dm^{-3} O_2, 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 TiO_2 (reaction 4 to 9) is predominant.

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

3.2. *The H_2SO_4/n-TiO_2 System*

Considering the above discussed effect of n-TiO_2 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} H_2SO_4) in the presence of 5 mg/ml n-TiO_2 powder were irradiated. In this case the light ($\lambda > 300$ nm) was practically absorbed by TiO_2 only, since the diluted sulfuric acid absorbs below 300 nm, whereby $\varepsilon_{300}(H_2SO_4) = 0.007$. 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 H_2SO_4/TiO_2 system delivered under illumination hydrogen and oxygen, the yields of which increased with the concentration of sulfuric acid as shown in Figure 4.

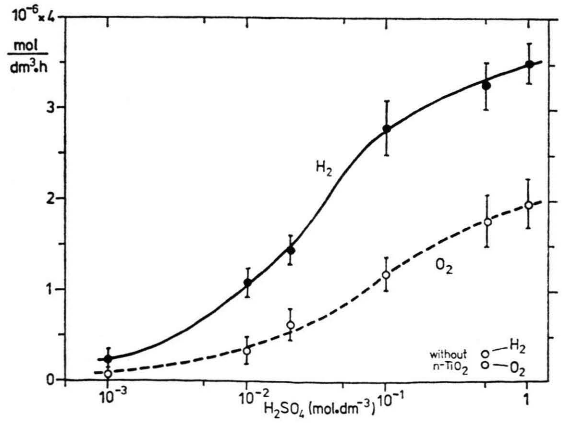

Fig. 4. H_2 and O_2 yields as a function of sulfuric acid concentration (Solution: 10^{-3} to 1 mol · dm^{-3} H_2SO_4, 5 mg/ml n-TiO_2; irradiation: 45 min at 30 °C).

It is of interest to note that the ratio of the H_2/O_2 yields is about 2. Based on this a consistent reaction mechanism is proposed. It is assumed that the $(TiO_2^+ \cdot e^-)$ 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-TiO_2 particles serves as an electron pool, where neutralization reactions take place.

$$(TiO_2^+ \cdot e^-) + H^+_{aq} \rightarrow H + TiO_2^+ , \quad (10)$$

$$H + H \rightarrow H_2 \quad (11)$$

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

$$H + H_2O \rightarrow H_2 + OH \quad (12)$$

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

By reaction (10) a very active n-TiO_2^+ surface is formed, which initiates O_2 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 H_2O to hydrogen and oxygen.

It is to be mentioned that, using 0.5 mol · dm^{-3} H_2SO_4 without addition of n-TiO_2 powder, very low yields for hydrogen ($\sim 0.3 \times 10^{-6}$ mol · dm^{-3} H_2) and oxygen ($\sim 0.2 \times 10^{-6}$ mol · dm^{-3} O_2) were obtained. This is due to the direct photolysis of the sulfuric acid, since [20]:

$$SO_4^{2-} \rightsquigarrow {}^*SO_4^{2-} \rightarrow \dot{S}O_4^- + e^-_{aq} , \quad (13)$$

$$e^-_{aq} + H^+_{aq} \rightarrow H \quad (14)$$

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

$$2\,\dot{S}O_4^- \rightarrow S_2O_8^{2-} . \quad (15)$$

Persulfuric acid is relatively by unstable and under illumination leads to O_2 formation and a mixture of sulforous and sulfuric acids. This process (reactions 13 to 15) can be supressed by using light with $\lambda > 350$ nm.

4. Conclusions

Experimental evidence is presented for the ability of illuminated ($\lambda > 300$ nm) n-TiO_2 suspension to act as a very efficient electron donor, which is regenerable under proper experimental conditions. A photoinduced oxidation of water is observed, when Ce^{4+} ions serve as electron acceptor in the presence of n-TiO_2. The O_2 yield is dependent upon temperature and the amount of added semiconductor. Using H^+_{aq} as electron acceptor and n-TiO_2 as electron donor the water is split to H_2 and O_2 under the influence of light.

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