Photoinduced CO-Reduction in Aqueous Suspension of n-TiO_2

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TiO_2-suspension as well as TiO_2-colloide in aqueous solutions are acting as catalyst for transforming CO into formaldehyde under illumination with uv-light. The yield of formaldehyde was studied as a function of pH (range: 1–7) and of the n-TiO_2 content in the suspension at pH 2. Probable reaction mechanisms are presented.

Introduction

The photoinduced transformation of aqueous carbon monoxide into formaldehyde, glyoxal, carboxylic acids and small amounts of glycol using vacuum-uv-light ($\lambda = 185$ nm) was reported very recently [1]. It was established that the quantum yield of these products strongly depends on the pH. Further, the photolysis of aqueous formaldehyde in the presence of CO essentially diminishes and in addition the formation of glyoxal, formic and oxalic acids is observed [2]. The initial processes are based on the H and OH radicals resulting from the water photolysis at 185 nm. On the other hand it has been shown that water decomposition to H_2 and O_2 occurs by illuminating n-TiO_2 particles in form of acidified aqueous suspension with light of $\lambda \geqq 300$ nm [3, 4]. Using appropriate scavengers (e.g. ferri-ions, alcohol etc.) it was found that on the surface of n-TiO_2 H and OH species are formed as primary species of water splitting [5]. Similar processes can also take place on the surface of platinized TiO_2-particles or colloids [6, 7 and ref. therein]. Using p-Si plate electrodes and powders, Yamamura et al. [8] succeeded to reduce CO to formaldehyde. The p-Si electrodes were coated with either porphyrins or metals in order to avoid corrosion. By illuminating with a 500 W Xenon lamp (150 mW/cm^2) during 4–8 hr they obtained in acid solutions aldehyde yields of $0.39–0.86 \times 10^{-6}$ M. In the case of p-Si suspensions (acidified or containing ethanol) the yields were somewhat lower, namely $0.21–0.32 \times 10^{-6}$ M HCHO.

Based on these observations it appeared very promising to reduce CO in aqueous solution in the presence of finely pulverized n-TiO_2 under the influence of light of $\lambda \geqq 300$ nm. The problem is of special interest for an eventual utilization of CO produced in large amounts by combustion of fossil fuels.

Experimental

Preparation of Solutions

At least triply distilled water was used for the preparation of the solutions, which were saturated with high purity CO (1×10^{-3} M CO; Messer Griesheim, Austria) at 20 °C. As a catalyst two types of TiO_2 were used: colloide and fine powders. The TiO_2-colloids were prepared according to the method by Moser and Grätzel [9] by hydrolysis of $TiCl_4$. The obtained colloide possesses an absorption maximum at $\lambda = 415$ nm and $\varepsilon = 640$ cm^3 M^{-1} cm^{-1} [10]. TiO_2 powder (anatase, Fluka) was first heated for 60 min at 1150 °C in the presence of oxygen and then treated in H_2-atmosphere at 700 °C for 90 min. Due to this operations, an n-TiO_2 powder rutile structure is obtained. It was granulated and sieved. Only n-TiO_2 with a grain size $\leqq 0.06$ mm was used as suspension in aqueous solution. For adjustment of the pH, p.a. $HClO_4$ and NaOH (Merck) were used.

Light Sources and Actinometry

A low pressure Hg-lamp (Osram, HNS 10 W) with incorporated filter for absorping vuv-line (185 nm) provided a monochromatic uv-light with $\lambda = 254$ nm.

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The actinometry was carried out using a monochloric acetic acid-actinometer [11]. The intensity of the lamp, $I_0 = 5.0 \times 10^{17}\, h\nu \cdot ml^{-1}\, min^{-1}$, was controlled periodically and was found to be constant. As a second light source served a medium pressure Hg-lamp (Philips, HPK 125 W), which emits a number of lines (312.6/313.4, 334, 365.2/365.6/366.5, 405.8, 407.8, 435.4, 545.8, 576 and 578 nm). The light with $\lambda < 300$ nm was removed by a "Duran 60" glass filter.

Chemical Analysis

Formaldehyde was found to be the main product of the CO-reduction on the TiO_2 surface. For its determination in the presence of acetyldehyde, glyoxal, glyoxyl acid and formic acid the method by Hantz [12] was found to be the most suitable one. As reagent was used a solution containing 25 g ammonium acetate, 3 ml 100% acetic acid and 0.2 ml acetylacetone, filled up to 100 ml with triply distilled water. The solution is stable for more than one month when kept in a refrigerator. The analysis of formaldehyde was performed by adding 2 ml reagent to 5 ml sample and filling up to 10 ml with triply distilled water. Before analysis TiO_2 was removed from the irradiated solution by filtration. After keeping the mixture for 50 min at 37 ± 1 °C, and then 20 min at room temperature, the optical density was measured against a reference sample at $\lambda = 412$ nm ($\varepsilon_{412} = 8000\, cm^3\, M^{-1}\, cm^{-1}$) [11].

Results and Discussion

Irradiation with uv-Light $\lambda = 254$ nm

For this series of experiments n-TiO_2 powder (rutile, grain size ≤ 0.06 mm) was used as an aqueous suspension (0.5 to 5 mg TiO_2/ml). The CO-saturated solutions (1×10^{-3} M CO) were irradiated at 20 ± 1 °C (thermostat) under stirring in order to keep the suspension homogeneous. Formaldehyde was found as a main product, in addition to very small amounts of glyoxal and carboxylic acids. The HCHO-yield was first studied as a function of the uv-dose at pH 2 and 7. The obtained data are presented in Figure 1. The initial quantum yields (Q_i) were calculated from the tangent of curves A and B plotted through the zero of the coordinate system. Obviously, the Q_i(HCHO)-value is essentially higher in acid than in neutral media.

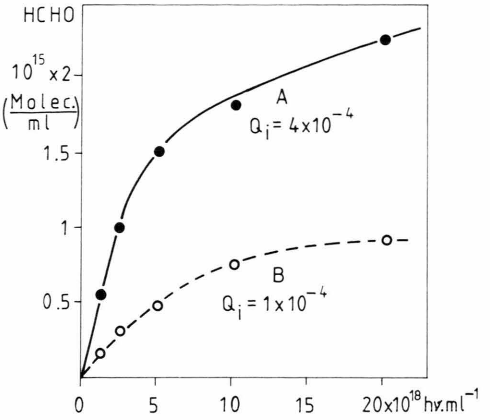

Fig. 1. Formation of formaldehyde from 1×10^{-3} M CO in an aqueous suspension of 1 mg TiO_2/ml as a function of uv-dose using uv-light with $\lambda = 254$ nm at pH 2 (A) and pH 7 (B).

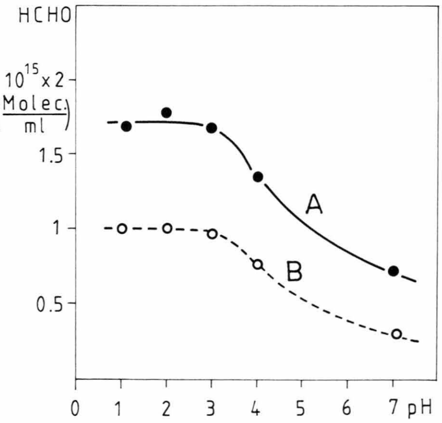

Fig. 2. pH-dependence of formaldehyde formation from 1×10^{-3} M CO in an aqueous suspension of 1 mg n-TiO_2/ml using uv-light with $\lambda = 254$ nm. Applied dose: $1 \times 10^{19}\, h\nu$/ml (A) and $2.51 \times 10^{18}\, h\nu$/ml (B). ($I_0^{254} = 5 \times 10^{17}\, h\nu/ml^{-1}\, min^{-1}$.)

This result initiated the study of the pH-dependence of the HCHO-formation under otherwise the same conditions. Figure 2 shows the rather strong decrease of the product yield in acid solutions from $Q_A = 1.7 \times 10^{-4}$ at pH 1 to 3 to $Q_A = 0.7 \times 10^{-4}$ at pH 7. The corresponding Q-values for curve B are 1×10^{-4} and 0.3×10^{-4}, respectively.

In addition to this, an interesting aspect represents the formation of HCHO as a function of the TiO_2-content in the CO-saturated suspension. This correlation is pictured in Fig. 3 for two uv-doses at pH 2. In both cases the aldehyde formation is linear with the

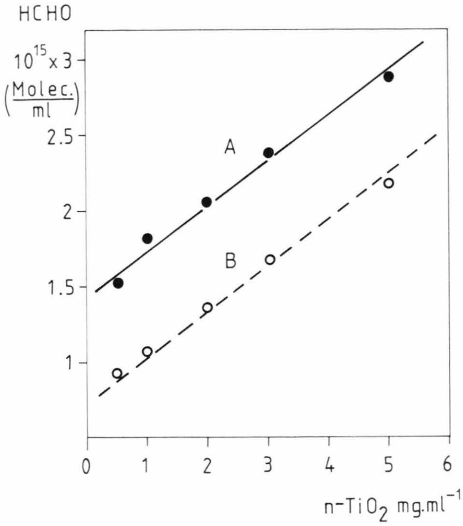

Fig. 3. Formaldehyde formation from 1×10^{-3} M CO vs. n-TiO_2-content in the suspension (pH 2) using uv-light with $\lambda = 254$ nm at an uv-dose of 1×10^{19} $h\nu$/ml (A) and 2.51×10^{18} $h\nu$/ml (B) respectively.

concentration of n-TiO_2 in the solution and in unison with the applied dose.

Irradiation with Medium Pressure Hg-Lamp (HPK 125 W)

As mentioned above, this lamp emits light with various wavelengths, most of which are practically absorbed by the n-TiO_2-colloid or fine particles, respectively. Both, colloids and particles are able to reduce CO under the present conditions. Further, it was established that with rising the pH of the solutions the formaldehyde yield decreases rapidly. In Fig. 4 some results from CO/n-TiO_2 particles system at pH 2 are presented. Curve A illustrates the fact that above a certain light dose (>40 min irradiation time) the aldehyde yield remains constant. This indicates the occurrence of back reactions on the catalyst surface. The strong pH-dependence of the aldehyde yield is demonstrated by curve B. It might be mentioned that in alkaline solutions (pH > 9) no formaldehyde was detectable.

Discussion

By immerging of an n-type semiconductor in an aqueous electrolyte a band-bending takes place and under illumination electrons are rised from the valence-band (E_V) to the conduction band (E_C) [13, 14]. The energy difference between both levels (band gap, E_G in eV) is a characteristic value for each kind of semiconductor. In the case of n-TiO_2, $E_G = 3.1$ eV, which corresponds to a light with $\lambda \cong 400$ nm. The applied low pressure Hg-lamp emitts $\lambda = 254$ nm, which corresponds to 4.8 eV/$h\nu$, whereas the medium pressure Hg-lamp provides energies from 2.13 eV/quant ($\lambda = 578$ nm) to 3.9 eV/quant (312.6 nm). Hence, it is obvious that when using the second lamp the light with $\lambda > 430$ nm is practically not utilized.

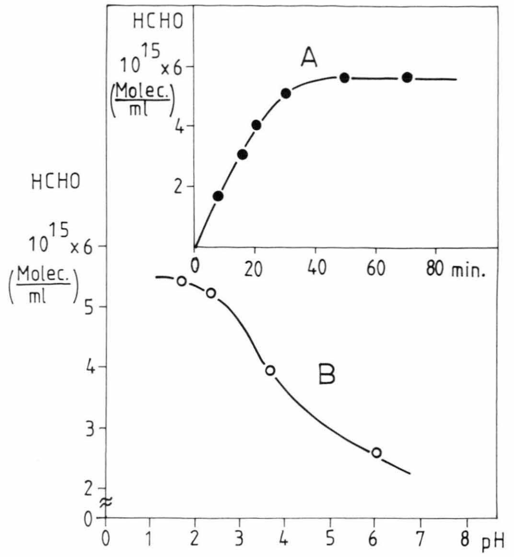

Fig. 4. (A) Formaldehyde formation as a function of irradiation time (HPK, 125 W-lamp) using CO-saturated aqueous solution (pH 2) in the presence of 1 mg n-TiO_2/ml. (B) pH-Dependence of the aldehyde yield obtained under the same experimental conditions (irrad. time: 30 min).

By illumination of n-TiO_2 aqueous suspension the following reactions take place:

$$TiO_2 \xrightarrow{h\nu} {}^*TiO_2 \longrightarrow (e^- \cdot TiO_2^+) \longrightarrow e^- + TiO_2^+ . \quad (1)$$

The system ($e^- \cdot TiO_2^+$) is identical with ($e^- \cdot p^+$), where p^+ (positive holes) corresponds to TiO_2^+, which is acting as oxidizing agent. The electrons on the surface of the TiO_2-particles can diffuse away and become solvated:

$$e^- + nH_2O \longrightarrow e_{aq}^- \quad \text{(solvated electrons)}. \quad (2)$$

The solvated electrons (e_{aq}^-) as well as e^- on the semiconductor-surface are able to react with H^+ in acid aqueous solution, resulting in H-atoms:

$$(e^- \cdot TiO_2^+) + H_{aq}^+ \rightarrow H + TiO_2^+ , \quad (3)$$

$$e_{aq}^- + H_{aq}^+ \rightarrow H \ (k = 2.3 \times 10^{10}\ M^{-1} s^{-1}\ [15]). \quad (4)$$

Both types of reducing species, electrons as well as H-atoms, can react with CO producing CHO-transients:

$$(e^- \cdot TiO_2^+) + CO \rightarrow CO^- + TiO_2^+ , \quad (5)$$

$$e_{aq}^- + CO \rightarrow CO^- \ (k = 1 \times 10^9\ M^{-1} s^{-1}\ [16]), \quad (6)$$

$$H_{aq}^+ + CO^- \rightarrow CHO , \quad (7)$$

$$H + CO \rightarrow CHO \ (k = 3.8 \times 10^8\ M^{-1} s^{-1}\ [17]), \quad (8)$$

The reactions (3) and (5) as well as (4) and (6) are competing processes.

The CHO-radicals can lead to the formation of formaldehyde or to some extent glyoxal.

$$2\,CHO \begin{cases} \rightarrow CO + HCHO\ \text{(formaldehyde)} & (9\,a) \\ \rightarrow (CHO)_2\ \text{(glyoxal)}. & (9\,b) \end{cases}$$

At low CO-concentrations the primary species, e_{aq}^- and H, can combine with each other producing hydrogen:

$$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2\,OH^- \ (k = 5 \times 10^9\ M^{-1} s^{-1}\ [18]), \quad (10)$$

$$H + H \rightarrow H_2 \ (k = 1 \times 10^{10}\ M^{-1} s^{-1}\ [19]), \quad (11)$$

$$e_{aq}^- + H \rightarrow H_2 + OH^- \ (k = 2.5 \times 10^{10}\ M^{-1} s^{-1}\ [20]). \quad (12)$$

The yield of hydrogen was not studied in this work.

On the other hand, the positive holes (p^+ resp. TiO_2^+) are able to oxidize water or to produce OH radicals depending upon the pH of the solution:

$$TiO_2^+ + H_2O \rightarrow TiO_2 + O_2 + H^+ , \quad (13)$$

$$TiO_2^+ + OH^- \rightarrow TiO_2 + OH . \quad (14)$$

The OH-radicals are reacting with CO forming $\dot{C}OOH$ radicals in competition with OH recombination:

$$CO + OH \rightarrow COOH \ (k = 8.3 \times 10^8\ M^{-1} s^{-1}\ [21]) , \quad (15)$$

$$COOH + COOH \begin{cases} \rightarrow HCOOH + CO_2 & (16\,a) \\ \rightarrow H_2C_2O_4\ \text{(oxalic acid)}, & (16\,b) \end{cases}$$

$$COOH \rightleftharpoons CO_2^- + H^+ \ (pK = 1.4\ [22]), \quad (17)$$

$$OH + OH \rightarrow H_2O_2 \ (k = 6 \times 10^9\ M^{-1} s^{-1}\ [19]). \quad (18)$$

Since the OH-species are mainly adsorbed on the semiconductor surface they seem to recombine (reaction (18)), rather then to form acids (reaction (15) and (16)), because only traces of formic acid could be detected.

The appearance of H_2O_2 explains at least partly the decomposition of formaldehyde at higher uv-doses (see Fig. 1 and Figure 4 A).

The lack of formaldehyde formation in alkaline solution could be explained by the formation of O-atoms, which decompose the eventually formed organic compounds:

$$OH \rightleftharpoons O^- + H^+ \ (pK = 11.8\ [23]), \quad (19)$$

$$(e^- \cdot TiO_2^+) + O^- \rightarrow e_{aq}^- + TiO_2 + O^{\bullet} . \quad (20)$$

It is worth to be mentioned that using n-TiO_2 powder in the presence of 1×10^{-3} M CO in aqueous acid solution (pH = 2; see Fig. 1) the obtained formaldehyde yield at $\lambda = 254$ nm is several orders of magnitude higher (1.6 M HCHO for 8 hr irradiation, based on $Q_i = 4 \times 10^{-4}$) than the previously reported one [8] of 0.32×10^{-6} M HCHO after 8 hr irradiation time. The aldehyde yield obtained in the present work under the influence of the HPK 125 W-lamp for the same irradiation time amounts to 1.6×10^{-4} M HCHO (see Fig. 4, curve A).

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