



The catalytic effects of copper ions on photo-oxidation in TiO₂ suspensions: The role of superoxide radicals

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ABSTRACT

UV photolysis of aerated aqueous suspensions of TiO₂ (Degussa P25) containing CH₃OH at pH 8.5 produces HCHO. Addition of CuSO₄ affects the rate of HCHO formation (R_{HCHO}) in two opposite ways. Below 2 μM, R_{HCHO} increases with increasing [CuSO₄] while at higher concentrations it slows down. The enhancement of R_{HCHO} at very low [CuSO₄] is attributed to catalytic dismutation of O₂^{•−} forming H₂O₂ and O₂. At higher [CuSO₄], R_{HCHO} decrease is attributed to removal of mobile holes by copper. Square root dependency of HCHO yield on the absorbed light density is observed in the entire [CuSO₄] range used. The square root dependency is generally attributed to competition between second-order electron–hole recombination and first-order trapping, although the lifetime of both electrons and holes is too short to enable their accumulation in the same nano-volume. It is shown here that the electron–hole recombination path involves reaction of the mobile holes with adsorbed O₂^{•−}. The experimental results provide indirect evidence that adsorbed O₂^{•−} radical ions, which are produced via O₂ reaction with the TiO₂ electrons, are important for the well known square root dependency. Unlike the mobile and trapped electrons, O₂^{•−} has a relatively long lifetime and its accumulation in the nano-volume upon successive absorptions of photons is feasible. It is concluded that the reaction between the accumulated O₂^{•−} and mobile holes is responsible for the square root law. The decrease of K_d , which has been suggested as a standard parameter for the nature of TiO₂ by added Cu(II) implies an apparent improvement of the TiO₂ quality as a photocatalyst.

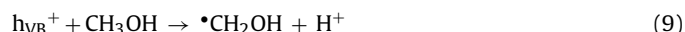
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1. Introduction

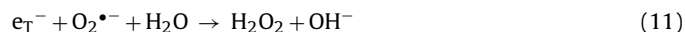
It is well known that light absorbed by a semiconductor nano-material such as TiO₂ produces a pair of a valence band hole, h_{VB}^+ , and a conduction band electron, e_{CB}^- (reaction (1)), which are readily trapped at the surface forming less mobile states (reactions (2) and (3)) in parallel to several recombination processes (reactions (4)–(7)) [1–9].



If a solute reacts with trapped holes at the surface, e.g. CH₃OH, the oxidation yield increases upon increasing the solute concentration due to the competition with the electrons for trapped holes (reaction (8) competing with (6) and (7)). If CH₃OH reacts with the shorter lived valence band holes (reaction (9)), the oxidation yield is affected also by the competition of reaction (9) with reactions (2), (4) and (5).



O₂ reacts with surface localized electrons yielding O₂^{•−} (reaction (10)), which can react with both electrons and holes (reactions (11) and (12)) although the rates are not known.



Besides the physico-chemical properties of TiO₂ nano-crystals, its photocatalytic activity depends on the substrate and the experimental conditions, such as adsorption of the substrate, pH and absorbed light density, I_d (einstein s^{−1} g^{−1} TiO₂). The effect of I_d

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on the photo-product quantum yield Φ has been studied by many researchers often showing a square root dependency of the rate of product build-up on I_d [10–39]. The square root dependency expressed by Eq. (13) is generally attributed to the competition between electron and hole trapping (Eqs. (2) and (3)) and their recombination (reactions (4)–(7)) [40].

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\max}} + \frac{K_d I_d^{1/2}}{\Phi_{\max}} \quad (13)$$

Since Φ varies with I_d , Eq. (13) is applicable only if I_d is uniform in the illuminated volume. When reaction (8) successfully competes with reactions (6) and (7) so that practically all the trapped holes react with the CH_3OH , the constant K_d is directly related to the photocatalytic efficiency of the TiO_2 at a given pH and O_2 concentration. This parameter is property of the TiO_2 and does not depend on the specific experimental conditions such as light intensity, wavelength, and thickness of the active medium [23].

Earlier works have shown that doping TiO_2 with Cu(II) enhance the rate of photo-oxidation of methyl orange. This has been attributed to electron-trapping forming Cu(I) or Cu(0), which have been claimed to inhibit electron–hole recombination [41]. Similarly, addition of 10–500 mM Cu(II) to TiO_2 suspensions in acid pH showed a remarkable effect on the photocatalytic oxidation of toluene [42], and on the rate of the photo-oxidation of carboxylic acids by oxygen [43]. The carboxyl-oxidation was attributed to the formation of specks on which the rate is different from the rate on the bare TiO_2 surface [44], and to carboxylato complexes of copper [45]. Butler and Davis [46] reported that Cu(II) increased remarkably the photocatalytic oxidation of phenol in TiO_2 suspensions at pH 3 even at a concentration as low as 1 μM . Higher concentrations were reported to have a detrimental effect. A complex between Cu(II), oxygen species (H_2O_2 or $\text{O}_2^{\bullet-}$) and the organic substrate in the bulk of the aqueous phase has been proposed. Suppression of photo-oxidation by addition of Cu(II) has been verified also by other laboratories. Wei et al. [47] reported retardation of phenol photo-oxidation by 10 mM Cu(II) (pH 4) although in the presence of added H_2O_2 pronounced enhancement was observed. Suppression of the photocatalytic oxidation of Imazapyr by up to 0.3 mM Cu(II) was attributed to enhanced electron–hole recombination in competition with the desired electron- and hole-reactions, to photodeposition of Cu(0) and Cu_2O at the TiO_2 surface, and to formation of neutral complex structures of Cu(II) with Imazapyr in the suspensions [48].

A previous study [23] noted that the square root dependency is observed even when only 0.15–3 electron–hole pairs per second are produced in the same TiO_2 particle in the entire intensity range studied. It was suggested that secondary products such as $\text{O}_2^{\bullet-}$ and H_2O_2 , which possess much longer lifetime than e_1^- , might be involved. The present study tests this hypothesis via the effect of catalytic amounts of Cu(II), a known catalyst for $\text{O}_2^{\bullet-}$ dismutation [49], on the rate of TiO_2 mediated CH_3OH photo-oxidation. CH_3OH has been chosen because its oxidation chemistry is simple and no formation of intermediate complexes such as in the phenol or Imazapyr systems is possible. The selected low level of Cu(II) assures that only a negligible fraction of the TiO_2 surface area can be considered “modified” and the role of Cu(II) must be related to its chemistry. The results provide additional insight into the mechanism of the square root dependency of the rate of product build-up on I_d .

2. Experimental

All solutions were prepared with de-ionized water, which was purified using a Milli-Q water purification system. TiO_2 (Degussa P-25), methanol (100%, Bio Lab, AR-b grade), sodium phosphate dibasic (Sigma, Reagent grade), copper sulfate (Riedel-De-Haen,

Puriss.), ammonium acetate (Sigma–Aldrich 98% grade), acetic acid (Frutarom, Analytical), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Riedel-De-Haen), acetylacetone (Sigma), diethylenetriaminepenta-acetic acid (DTPA) (Sigma) and biscyclohexanone-oxalyldihydrazone (cuprizone) (BDH chemicals) were used without further purification.

The concentration of formaldehyde was determined using the Nash reagent (2 M ammonium acetate, 0.05 M acetic acid, 0.02 M acetylacetone) [50]. We found that under the conditions of the present work about 10% HCHO is adsorbed by TiO_2 . Therefore, the reagent was added prior to the removal of TiO_2 by centrifugation. Control tests showed negligible, if any adsorption of the HCHO–acetylacetone complex.

The concentration of H_2O_2 was determined by the molybdate-activated iodide assay [51]. Stock aqueous suspensions of TiO_2 (10 g/L) were daily prepared and used after 20 min of sonication. TiO_2 was removed prior to the analysis by centrifugation. The adsorption of Cu(II) to TiO_2 was studied using cuprizone, which is an efficient chelator of Cu(II) with relatively high absorption at 600 nm [52,53]. Cuprizone stock solution of 0.02 M was prepared in 50% (volume) CH_3OH water solution. A given concentration of CuSO_4 was vigorously mixed with 0.25 g/L TiO_2 suspension containing 2 M CH_3OH and 1 mM Na_2HPO_4 . After 20 min, which proved to be sufficient for equilibration, the TiO_2 was removed by centrifugation. The remaining clear solution was tested for copper by adding Na_2HPO_4 (5 mM), KCl (0.1 M) and cuprizone (1 mM), maintaining the temperature at 55 °C until a constant absorbance was observed after about 30 min. Absorbance was measured in a 2 or 4 cm cell at 20 °C, and the [Cu(II)] derived from a calibration line. The absorbance is directly proportional to the added [CuSO₄], corresponding to $\epsilon_{600} = 16,000 \text{ M}^{-1} \text{ cm}^{-1}$.

2.1. Photolysis

The light source was a Xenon lamp (Osram 150 W ozone free) coupled with a monochromator (SX-17MV setup from Applied Photophysics). The slits of the monochromator were usually fully open (10/10 mm) transmitting a band with of about 40 nm. In a few cases 9/6 mm slits were used. Illuminations were usually carried out at 330, and in some cases at 320 nm. Measurements of the so called “monochromator scattered light” (unfiltered light passing through the monochromator by reflections) was carried out by comparison between the light-signal at the given wavelength to that at 170 nm. Since the light at 170 nm is absorbed by the air, any light signal at this wavelength must be attributed to light from higher wavelengths scattered inside the monochromator, which was negligible above 300 nm.

Illuminations were carried out in a four windows cuvette with dimensions 1 cm × 1 cm and height 4 cm, made from quartz under vigorous magnetic stirring at room temperature (24 ± 1 °C). The incident light intensity was measured with a sensitive calibrated Si photo-sensor (Hamamatsu S2281) coupled with a programmable electrometer (Keithley 617). The light passed through an aperture 9 mm diameter to ensure that the beam incident is smaller than the dimensions of both cuvette and radiometer. The total illuminated solution volume was usually 3 mL, although in several cases 1.7 mL resulted in the same intensity profile as 3 mL indicating efficient mixing.

3. Results

HCHO is formed upon irradiation of TiO_2 suspensions containing O_2 , CH_3OH and 1 mM HPO_4^{2-} (pH 8.5) according to reactions (8), (9), (14) and (15) [23]. The build-up of HCHO was linear with the illumination time, demonstrating that reactions of HCHO with the photolytic transients were not important. Note that the species involved in reactions (14)–(17) may adsorb to TiO_2 and therefore

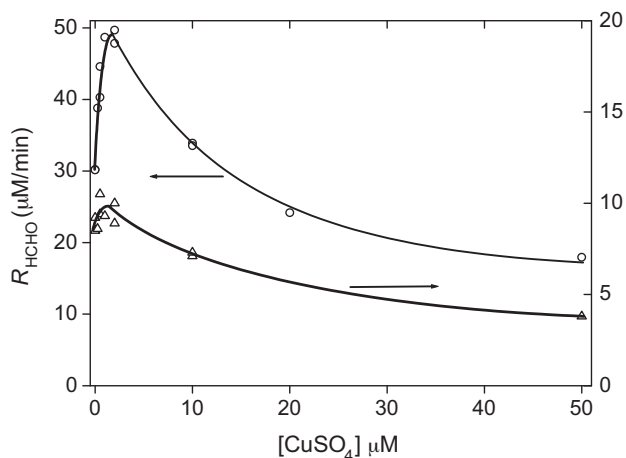
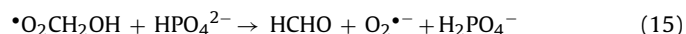
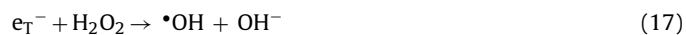
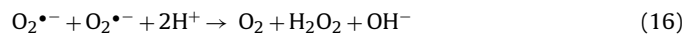


Fig. 1. The effect of $[\text{CuSO}_4]$ on R_{HCHO} at I_d (O) $3.2 \times 10^{-4} \text{ einstein g}^{-1} \text{ min}^{-1}$ (left scale) and (Δ) $4.0 \times 10^{-5} \text{ einstein g}^{-1} \text{ min}^{-1}$ (right scale). Aerated suspensions of 0.25 g/L TiO_2 containing 2 M CH_3OH and 1 mM Na_2HPO_4 (pH 8.5) were illuminated (330 nm) for 4–15 min.

the rates of reactions (14)–(17) are influenced by their adsorption/desorption. Since we are unable to discriminate between the different contributions, reactions (14)–(17) present both bulk and adsorbed species.



$\text{O}_2^{\bullet-}$ ($\text{p}K_a = 4.8$ [54,55]) produced by reactions (10) and (15) dismutates yielding O_2 and H_2O_2 (reaction (16)), where H_2O_2 is reduced by e_1^- forming $\bullet\text{OH}$ (reaction (17)).



A limiting quantum yield of nearly 2 had been reported for HCHO upon extrapolation to zero I_d according to Eq. (13) [23]. The constant K_d , which can be determined experimentally from the slope and intercept of the line representing $1/\Phi$ vs. $I_d^{1/2}$, has been suggested as a measure of the relative efficiency of trapping compared to recombination for the specific photocatalyst [23].

3.1. The effect of Cu(II) on the rate of HCHO build-up

The effect of $[\text{CuSO}_4]$ on the rate of HCHO build-up (R_{HCHO}) is shown in Fig. 1 for two absorbed light densities. At $[\text{CuSO}_4] < 2 \mu\text{M}$ and $I_d = 3.2 \times 10^{-4} \text{ einstein g}^{-1} \text{ min}^{-1}$, R_{HCHO} increases considerably with increasing $[\text{CuSO}_4]$ in contrast to the results at $4.0 \times 10^{-5} \text{ einstein g}^{-1} \text{ min}^{-1}$, which show only a small change. At $[\text{CuSO}_4] > 2 \mu\text{M}$, R_{HCHO} decreases with increasing $[\text{CuSO}_4]$ and the relative decrease does not depend on I_d .

Fig. 2 presents the well known linear dependency of $1/\Phi_{\text{HCHO}}$ on $I_d^{1/2}$ (Eq. (13)) in the absence and presence of $2 \mu\text{M}$ CuSO_4 . The results demonstrate that both slope and intercept, related to K_d and Φ_{max} , are affected by $0.25 \mu\text{M} < [\text{CuSO}_4] < 50 \mu\text{M}$. The dependence of K_d and Φ_{max} on $[\text{CuSO}_4]$, which is obtained using average values from plots such as in Fig. 2, is shown in Figs. 3 and 4, respectively. Fig. 3 also demonstrates that K_d depends only little, if at all, on $[\text{CH}_3\text{OH}]$. In the absence of added CuSO_4 , an average $K_d = (470 \pm 100) \text{ einstein}^{-1/2} \text{ s}^{1/2} \text{ g}^{1/2}$ is obtained for air saturated suspensions containing 2–5 M CH_3OH . This value is considerably lower than that measured for a layer, $K_d = 1500 \text{ einstein}^{-1/2} \text{ s}^{1/2} \text{ g}^{1/2}$ [23].

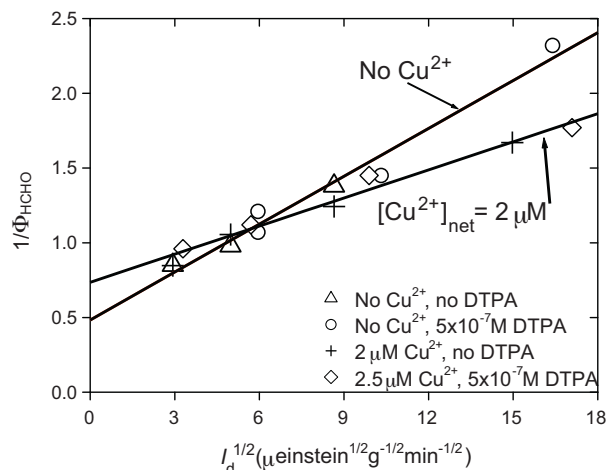


Fig. 2. The square root dependency of $1/\Phi_{\text{HCHO}}$ vs. I_d . Aerated suspensions of 0.25 g/L TiO_2 containing 2 M CH_3OH and 1 mM Na_2HPO_4 (pH 8.5) were illuminated (330 nm) for 2.5–25 min. Note that in the presence of $0.5 \mu\text{M}$ DTPA and $2.5 \mu\text{M}$ Cu(II) the “free” Cu(II) concentration is $2.0 \mu\text{M}$.

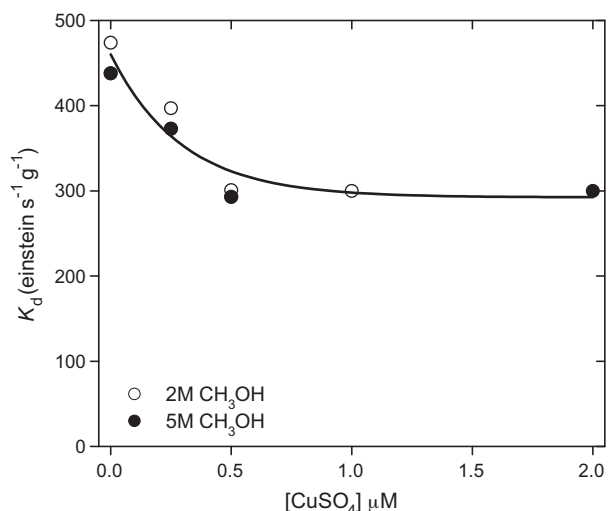


Fig. 3. Effect of $[\text{CuSO}_4]$ on K_d . Aerated suspensions of 0.25 g/L TiO_2 containing 1 mM Na_2HPO_4 (pH 8.5) and (O) 2 M or (●) 5 M CH_3OH were illuminated at 330 nm.

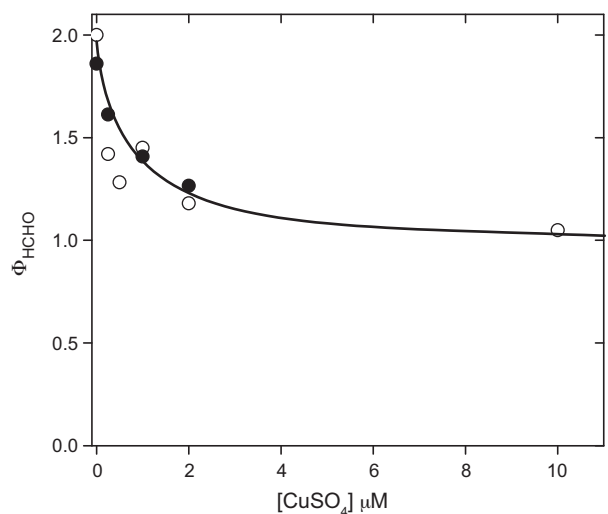


Fig. 4. Effect of $[\text{CuSO}_4]$ on the limiting Φ_{HCHO} . Aerated suspensions of 0.25 g/L TiO_2 containing 1 mM Na_2HPO_4 (pH 8.5) and (O) 2 M or (●) 5 M CH_3OH were illuminated at 330 nm.

3.2. Adsorption of Cu(II) to TiO₂

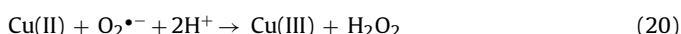
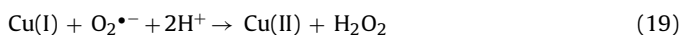
Adsorption of copper species to TiO₂ has been reported previously [56,57]. Our measurements show less than 0.2 μM Cu(II) in the bulk after equilibration of 10 and 20 μM CuSO₄ with 0.25 g/L TiO₂. Addition of cuprizone to the solid TiO₂, which was separated from the solution after equilibration with CuSO₄, demonstrated strong copper–cuprizone absorption. These results show that practically all the copper was adsorbed to the TiO₂.

4. Discussion

4.1. Increasing R_{HCHO} at [CuSO₄] < 2 μM

Eq. (13) is generally attributed to the competition between reactions (2) and (3) with the recombination reactions (4)–(7). The extrapolated value of 1/Φ_{HCHO} = 0.5 (Fig. 2, no Cu(II)) corresponds to a limiting Φ_{HCHO} = 2, implying that practically all the trapped holes and electrons eventually give rise to HCHO. This result rules out an effect of organic contaminants (if present) in the system. CH₃OH reacts with h_T⁺ (reaction (8)) but not with h_{VB}⁺ (reaction (9)). This is evident from the limiting values of Φ_{HCHO} observed at high [CH₃OH], which are much lower than 2 at high I_d, and is shown by the lack of a significant effect of [CH₃OH] on K_d or Φ_{max} (Figs. 3 and 4). Since the rate of reaction (3) is very fast and at the high [CH₃OH] used in this work, h_T⁺ is nearly completely converted to •CH₂OH (reaction (8)), the recombination reactions (4), (6) and (7) can be ignored. Pulse radiolysis studies of TiO₂ particles (4.7 nm average diameter) in colloid solutions have shown that reaction (10) has four-exponential steps with 80% of the electrons decaying in three exponential steps with a half-life less than 30 ms in air saturated solutions [58]. The fraction of the faster reactions and their rates tends to increase with increasing particle size [58]. The lifetime of e_T⁻ in the aerated suspensions is short compared to the frequency of successive absorption of a photon by the same particle [23]. Hence, reaction (5) cannot account for the square root dependency since most e_T⁻ are converted to O₂^{•-} and cannot accumulate on the same nano-crystal. On the other hand, O₂^{•-} produced by reactions (10), (14) and (15) has relatively long lifetime and may accumulate and compete for the mobile holes. This means that the “electrons”, which are involved in electron–hole recombination are in fact O₂^{•-}, apparently adsorbed at the TiO₂ surface. This explains not only the accumulation of more than one “electron” per particle, which is essential for the square root law, but also the increase of R_{HCHO} by traces of copper.

The concentration of the produced HCHO exceeds that of the added CuSO₄ by 1–2.5 orders of magnitude, and therefore the role of copper in this system is catalytic. Reactions (18)–(21) between the adsorbed copper species and adsorbed O₂^{•-} describe the dismutation of O₂^{•-} [49]. Note that Cu(I), Cu(II) and Cu(III) in Eqs. (18)–(21) represent adsorbed species. The actual mechanism is more complicated since CuO₂⁺ may be formed as an intermediate via reaction (18) [59,60]. In view of the high redox potential of the Cu³⁺/Cu²⁺ couple [61], the catalytic redox pair cannot be Cu²⁺/Cu³⁺ in the bulk. However, copper quantitatively adsorbs to the TiO₂ forming copper hydroxide species, which dominate at pH > 5 [57]. Apparently, the redox potential of the adsorbed couple is lower compared to the respective bulk species [62] and the oxidation of Cu(II) to Cu(III) at the TiO₂ surface may be feasible.



Lowering the steady state level of O₂^{•-} favors trapping of h_{VB}⁺ and consequently increases R_{HCHO}. Addition of 0.5–12.5 μM DTPA in the absence of CuSO₄ decreases Φ_{HCHO} by approximately 7%. This is attributed to the removal of traces of metals, which are often present in the system and catalyze O₂^{•-} dismutation. Indeed, the effect of added CuSO₄ can be completely titrated by DTPA and the CuSO₄ effect can be completely eliminated by a slight excess of DTPA. These results are in agreement with the proposed electron–hole recombination path, as the DTPA–Cu(II) complex does not catalyze O₂^{•-} dismutation [63].

4.2. Decreasing R_{HCHO} at [CuSO₄] > 2 μM

Above 2 μM CuSO₄ R_{HCHO} decreases (Fig. 1). Reduction of Cu(II) by the TiO₂ electrons (reactions (22) and (23)) cannot account for this effect.

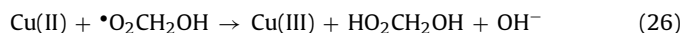


Reaction (22) can be ruled out because of the very fast electron trapping (reaction (3)) [45]. A question arises as to the possible role of reaction (23). The reduction potentials of Cu(OH)₂ to Cu(0) or Cu₂O (ε⁰ = –0.222 or –0.080 V, respectively [61]) suggest that two-electron reduction by e_T⁻ is thermodynamically feasible. Photo-reduction of Cu(OH)₂ to Cu(0) on TiO₂ surface has been recently reported in deaerated suspensions [64], although Cu(0) freshly produced on TiO₂ surface is readily re-oxidized to Cu(II) upon admission of air [65]. One-electron reduction of Cu(OH)₂ to Cu(OH) is less likely and was not observed [64]. Therefore, in our system, where the presence of oxygen interferes with the accumulation of electrons, reaction (23) is not likely to be important. In any case, reduction of Cu(II) by e_T⁻ (reaction (23)) or by a two-electron reduction reaction in competition with the multi-stage reaction (10) [58] provides a parallel path for O₂ reduction without retarding R_{HCHO}. Promotion of electron–hole recombination and consequently slowing down HCHO build-up is expected if oxidation of adsorbed Cu(II) by the holes (reactions (24) and (25)) is followed by oxidation of O₂^{•-} by the produced Cu(III) (reaction (21)).



Wang and Wan [66] showed that reduction of Cu(II) to Cu(0) takes place upon illumination of deaerated suspensions of TiO₂ in the presence of both CH₃OH and Cu(II). This observation can be accommodated with reactions (24) and (25) if the produced Cu(III) reacts with CH₃OH in the deaerated suspension [60]. In contrast, under our experimental conditions O₂^{•-} builds up and successfully competes with CH₃OH for Cu(III).

If the reaction Cu(II) with •O₂CH₂OH takes place (reaction (26)), it may also lead to Cu(III) formation along with the hydroperoxide HO₂CH₂OH. The latter is known to decompose slowly yielding HCHO and H₂O₂.



In order to account for the decrease of R_{HCHO}, the formation of Cu(III) must be followed by its reduction according to reaction (21), converting O₂^{•-} into O₂. This reaction path is not likely in view of the fairly fast reaction (15) (k₁₅ = 2 × 10⁶ M⁻¹ s⁻¹) [67] and the reported slowness of Cu(II) reaction with the peroxy radical derived from ethanol [68]. The observed retardation of R_{HCHO} implies that Cu(III) is reduced by O₂^{•-} and not by CH₃OH. In conclusion, Cu(II) oxidation by either holes or •O₂CH₂OH, which is followed by subsequent reaction of Cu(III) with O₂^{•-}, leads to inhibition of HCHO formation.

There is an apparent contrast between the pronounced increase of R_{HCHO} by added Cu(II) (<2 μM) at

$I_{\text{abs}} = 3.2 \times 10^{-4} \text{ einstein g}^{-1} \text{ min}^{-1}$ and the only small effect when $I_{\text{abs}} = 4.0 \times 10^{-5} \text{ einstein g}^{-1} \text{ min}^{-1}$ (Fig. 1). Fig. 2 shows that addition of $2 \mu\text{M}$ CuSO_4 decreases both the limiting quantum yield of HCHO (higher intercept) and K_d (lower slope). Accordingly, Cu(II) has two opposite effects; increasing R_{HCHO} by catalyzing $\text{O}_2^{\bullet-}$ dismutation and decreasing R_{HCHO} via the reaction of Cu(III) with $\text{O}_2^{\bullet-}$, amounting to the creation of additional paths for electron–hole recombination. The combination of a higher intercept with a lower slope means that the two lines of Fig. 2 must have an intersection point, which is determined by the kinetic parameters. The only small effect at $I_{\text{abs}} = 4.0 \times 10^{-5} \text{ einstein g}^{-1} \text{ min}^{-1}$ is not surprising since the absorbed light density is sufficiently close to the intersection of the two lines in Fig. 2.

In O_2 -saturated suspension K_d is about three times smaller than in aerated suspension and varies only little, if at all, upon Cu(II) addition. It is proposed that O_2 competes with $\text{O}_2^{\bullet-}$ for the TiO_2 adsorption sites. The higher $[\text{O}_2]$ may affect electron–hole recombination by converting electrons to $\text{O}_2^{\bullet-}$ radicals, which are replaced at the TiO_2 surface by the more concentrated O_2 . Removal of $\text{O}_2^{\bullet-}$ from the surface is apparently responsible for the small effect of added Cu(II), as enhancing $\text{O}_2^{\bullet-}$ dismutation does not have the same effect on increasing R_{HCHO} when the majority of $\text{O}_2^{\bullet-}$ are in the bulk.

4.3. K_d and the limiting Φ_{HCHO}

We have previously suggested the use of CH_3OH as a probe for comparison between different TiO_2 [69]. K_d has been thought to be a parameter related to the inherent properties of the titania and not to the specific experimental conditions and choice of the substrate. The advantage of using CH_3OH is the simplified mechanism when reaction (8) rather than reaction (9) represents the predominant oxidation path, despite the higher free energy change in reaction (9). Reaction (8) may be favored in H-abstraction reactions because h_{T}^+ , which is a localized oxidized surface state, e.g. Ti-O^{\bullet} or Ti-OH^{\bullet} [6], is capable to react similarly to free $\bullet\text{OH}$ radicals. On the other hand, h_{VB}^+ represents delocalized electron deficiency and therefore is likely to react via electron transfer. Reactions (8) and (9) may therefore represent different types of reactions with respect to organic materials, which favor H-abstraction although the schematic formulas are similar. In addition, the trapping of h_{VB}^+ (reaction (2)) may effectively compete with reaction (9) so that reaction (8) may become more important even if the mechanism involves electron transfer in both cases.

The separation between reactions (8) and (9) is the reason for the observation of product limiting quantum yield lower than 2 at absorbed light densities extrapolated to zero.

The competition between the first-order trapping and the second-order recombination reactions leads to the square root dependency between the rate of the product build-up and light intensity. As the recombination reaction involves $\text{O}_2^{\bullet-}$, it follows that the square root profile observed in many systems is a result of the presence of O_2 , which is a common solute in practically all TiO_2 photocatalytic systems. The results reported here, however, suggest that K_d as well as the limiting quantum yield may be affected by traces of metal impurities, calling for stricter definition of the experimental conditions under which these parameters are indeed properties of the TiO_2 preparation alone. In addition, the un-explained difference between the values of K_d in layer and in suspension limits comparative tests to similar media.

5. Conclusions

The square root law is widely rationalized as a competition between second-order electron–hole recombination and

first-order trapping. The second-order rate law is expected only when the illumination builds up a steady-state of at least several electrons or holes in the reaction volume. However, the overwhelming majority of the works involve steady-state photolysis, and the lifetimes of the TiO_2 electrons and holes are much too short to enable their accumulation in the nano-volume. The question arises as to the real nature of the recombining species, which are responsible for the square root dependency. Surprisingly, this question has been usually ignored. The square root law is generally discussed in terms of “electrons” and “holes” without addressing the nature of these species, although reactions of secondary intermediates e.g. $\text{Cl}_{\text{ads}}^{\bullet}$ with $\text{O}_2^{\bullet-}$ and electrons or $\text{O}_2^{\bullet-}$ with holes have been reported [70,71].

In the present study we show that very low concentrations of copper induce a considerable increase of the photo-product build-up rate, which is attributed to superoxide dismutation catalyzed by Cu(II). It is concluded that the recombination involves adsorbed $\text{O}_2^{\bullet-}$ and valence band holes. Although there cannot be more than one valence band hole in the nano-particle, accumulation of several $\text{O}_2^{\bullet-}$ radical ions, which are relatively stable, is sufficient to impose a second-order rate law.

The adsorption of both Cu(II) and $\text{O}_2^{\bullet-}$ to TiO_2 suggest that the role of added traces of copper is to convert $\text{O}_2^{\bullet-}$ into H_2O_2 and O_2 . Cu(II) can react directly with the TiO_2 electrons, but such a reaction has no effect on the concentration of $\text{O}_2^{\bullet-}$ since Cu(I) reacts rapidly with O_2 . This role of Cu(II) implies that $\text{O}_2^{\bullet-}$ is important in the mechanism of electron–hole recombination, which is responsible for the square root profile affecting the net yields of stable products.

The parameter K_d , which reflects the efficiency of recombination compared to hole-trapping under standard conditions, is typical for the photocatalyst. However, K_d may be affected by minute concentrations of catalytic impurities as shown by the addition of sub- μM levels of Cu(II). The decrease of K_d by added Cu(II) implies an apparent improvement of the TiO_2 quality as a photocatalyst. There is no contradiction between this effect and the parallel decrease of the limiting Φ_{HCHO} . The catalytic removal of $\text{O}_2^{\bullet-}$ enhances HCHO production, while oxidation of Cu(II) by mobile holes followed by its regeneration via Cu(III) reduction by $\text{O}_2^{\bullet-}$ amounts to catalytic enhancement of electron–hole recombination by the same redox pair. The overall result, promoting or retarding R_{HCHO} , is a function of the kinetic parameters and $[\text{Cu(II)}]$. Time resolved analysis of the light scattering system may provide the accurate kinetic constants, which are required for specific simulations and predictions.

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