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Role of Excess Electrons in TiO_2 Nanoparticles Coated with Pt in Reduction Reactions Studied in Radiolysis of Aqueous Solutions

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Surface modification of TiO_2 nanocrystallites in aqueous solution was carried out by reduction of chloroplatinic acid with TiO_2 electrons ($e_{TiO_2}^-$). The TiO_2 electrons had been generated through electron injection from 2-propanol radicals, hydrogen atoms, and hydrated electrons produced by γ or pulse radiolysis prior to the addition of the chloroplatinic acid. Upon addition of the latter, Pt^0 clusters are produced by multistep reduction of the chloroplatinic acid on the TiO_2 surface. The present work concerns the material balance and chemical kinetics of the Pt^0 mediated reduction of water and H^+ to molecular hydrogen by the TiO_2 electron. Pt^0 showed no effect on the rate of oxygen reduction, compared to bare TiO_2. The effect of surface Pt^0 on increasing photocatalytic yields, claimed by a number of laboratories, is apparently due to electron capture by the Pt^0 rather than electron removal by oxygen.

Introduction

Semiconductor−metal compositions have been widely used to enhance photocatalytic efficiencies, in particular platinizations of TiO_2 were used to improve photocatalytic yields and increase detoxification rates. Graetzel[1] has noted that free diffusion of charge carriers permits electron transfer within a time of 0.1 ps and thus effectively competes with electron−hole recombination. It has been recently shown (in the ZnO/Pt nanocrystallites, which has similar energy properties to TiO_2/Pt), that excess electrons reside exclusively on the Pt.[2] Thus, it is not surprising that the TiO_2/Pt system shows enhanced photocatalytic degradation of biphenol compared to bare TiO_2,[3,4] such as in oxidation of ammonia to N_2[5] and CO photooxidation.[6] Photoreduction was occasionally used for preparation of Pt−TiO_2. The interaction of Pt and TiO_2 was investigated by means of UV−vis absorption spectra, photoluminescence emission spectra, and X-ray photoelectron emission spectroscopy. Pt^0, Pt^{2+}, and Pt^{4+} on the surface of Pt/TiO_2, and the Ti^{3+} species existing in its lattice were proposed to form a defect energy level. It has been claimed that the overall yield of trapped holes can be considerably increased when small platinum islands are present on the TiO_2 surface, which act as efficient electron scavengers competing with the undesired e^-/h^+ recombination.[7,8] Platinum (or nitrogen) may also effectively convert titania into a semiconductor photocatalyst active in the visible.[9] A number of works have been published concerning photochemical generation of hydrogen in Pt modified TiO_2 surface.[10,11] Comparison of the photocatalytic activity for H_2 generation between Au−TiO_2 and Pt−TiO_2 in illuminated aqueous 5 M C_2H_5OH suspension showed that the overall activity of Au samples was generally about 30% lower than that of Pt samples.[10] The H_2 yield was found to depend on the metal content on TiO_2, with a maximum in the ranges 0.3−1 wt % Pt, and that the rate of H_2 production was strongly dependent on the initial pH of the suspension. Wang, Heller, and Gerischer[12] have shown that catalyzed oxygen reduction by surface metal increases photocatalytic oxidation yields by preventing accumulation of electrons on the TiO_2 particles, thus inhibiting the rate of electron−hole recombination. Incorporation of Pd^0 in the surface increased the quantum efficiency of the photoassisted oxidation of aqueous 2,2-dichloropropionate 3-fold at 0.01 wt % Pd.[12]

Reduction reactions of excess electrons in TiO_2 nanocrystallites produced by pulse radiolysis have been studied earlier.[13] Rates of reductions of several substrates were determined and it was found that the rates depend on the TiO_2 particle size. Cu^{2+}, ClO_2^-, ClO_3^-, NO_2^-, and NO_3^- showed decay of the TiO_2 electron predominately by a single pseudo-first-order process. On the other hand, hydrogen peroxide and oxygen show a multiexponential decay.

The purpose of the present work is to study the effect of surface coated Pt on TiO_2 electron reduction of oxygen, H^+ and water. We have studied the reactions of the TiO_2 electrons in the TiO_2/Pt system after the generation of the electrons had been completed, rather than during photolysis.[10,11] This enabled the elucidation of the reaction mechanism, radiation yields and kinetic rate constants, as well as separation between the reduction of H^+ and water.

Experimental Section

Colloidal TiO_2 solutions were prepared by hydrolysis of $TiCl_4$ (Aldrich 99.9%). As reported previously,[14] 25 mL of TiO_2 were introduced very slowly under a stream of argon and vigorous stirring into 700 mL of 0.1 M HCl solution cooled at 0 to 4 °C. After 30 min stirring at 0 °C, the solution was dialyzed against HCl solution at pH3 (pore size cutoff 6000−8000). TiO_2 concentrations were determined by spectrophotometric measurements at 215 nm using $\epsilon = 6050\ M^{-1}\ cm^{-1}$ (in terms of TiO_2 molecules). Concentrations in the range of 0.16−0.28 M were obtained as small particles (average diameter of about 1 nm) and kept in a refrigerator at 2−5 °C. By heating such suspension at 45 °C for 5 days, the size of the particles increased to a

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diameter of about 5 nm. The pH was adjusted with HCl. The results are given for the 5 nm diameter, unless otherwise stated.

Pulse Radiolysis. Linear electron beam accelerator (Varian 7715) operated at 5 MeV and 200 mA current with 1.5 μs pulse duration was used. Experiments were carried out in a 1 cm quartz cell (3 cm light path) and temperature (22 ± 2) °C at the maximum dose, yielding about 1.5×10^{-5} M reducing radicals per pulse (assuming $Ge_{aq}^- + G_{OH^\bullet} + G_{H^\bullet} = 6$, where G_x stands for the number of X molecules produced by 100 eV absorbed radiation). Dosimetry was carried out by measuring the 480 nm absorption of $(SCN)_2^{\bullet-}$ produced in 5 mM N_2O saturated SCN^- solution at neutral pH, using $\epsilon_{(SCN)_2^-} = 7600$ M^{-1} cm^{-1}. The absorption changes of the reactions of $e_{TiO_2}^-$ were monitored at 600 nm.

Preparation of Pt Coated TiO$_2$. A total of 5 mL of TiO_2 (0.16−0.2 M) containing 0.2 M 2-propanol were Ar saturated in a test tube sealed with a rubber septum and irradiated either by γ rays or electron beam to produce about 1 mM $e_{TiO_2}^-$. Under these conditions, the $e_{TiO_2}^-$ is very stable, but upon addition of chloroplatinic acid, a fast reaction takes place, reducing the platinum ions to the metallic form. An amount of H_2PtCl_6 solution ($[H_2PtCl_6] < [e_{TiO_2}^-]$) saturated with argon was injected through the septum to reach the desired concentration of the reduced platinum. Excess electrons remaining at the end of the reduction process were destroyed by exposure to oxygen.

Slow Kinetics. For measurements of reaction rates in the time range of several hours, solutions of TiO_2 colloid coated or uncoated with platinum were transferred into a quartz cell connected to a vacuum valve and argon was bubbled through a sidearm with the aid of a capillary polyethylene tubing for at least 20 min. After bubbling the valve was closed under a strong flow of argon and the cell was taken for electron beam irradiation receiving 30−40 consecutive pulses of about 30 Gy each to load the TiO_2 with excess $e_{TiO_2}^-$. Following the irradiation the cell was placed in a thermostated holder (25 °C) connected to a Hewlett-Packard diode array spectrophotometer for the kinetic measurements.

Hydrogen Determination. In each experiment, three test tubes containing 5 mL of argon saturated TiO_2 solutions coated with platinum were bubbled with oxygen to destroy any traces of $e_{TiO_2}^-$ and subsequently deaerated with argon. These solutions were irradiated again in a ^{137}Cs γ source for 2−3 h, receiving a total dose of (1.0−1.7) kGy. The irradiation was carried on together with three reference samples receiving exactly the same dose. The reference samples contained aqueous 2-propanol (0.2 M) in the absence of TiO_2/Pt at pH 2.5. The reference samples served for determination of the hydrogen yields by comparison between the hydrogen signals in the reference and in the TiO_2/Pt solutions. The test tubes were left at room temperature for 17−20 h to ensure completion of the reaction producing hydrogen. The test tubes were vigorously shaken before injecting a given volume from the gas phase to the HP-5890 gas chromatograph (TCD detector, Porapak column from Supelco and argon as the gas carrier). Calibration of peak areas versus injected volumes of H_2/Ar mixtures showed linear response to H_2.

Results and Discussion

The primary radicals and molecules produced in water upon electron-beam pulse or γ irradiation are shown on the right-hand side of eq 1. The numbers in parentheses represent the respective *G* values

$$H_2O \rightarrow e_{aq}^-(2.7),\ OH^\bullet(2.7),\ H^\bullet(0.6),\ H_2(0.45),\ H_2O_2(0.7) \qquad (1)$$

In the presence of 2-propanol, the $OH^\bullet$ and $H^\bullet$ radicals abstract hydrogen from the alcohol to produce the 2-propanol radical $(CH_3)_2C^\bullet OH$ as shown in reactions 2 and 3

$$OH^\bullet + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2C^\bullet OH \qquad (2)$$

$$H^\bullet + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2C^\bullet OH \qquad (3)$$

In the absence of oxygen and H_2PtCl_6, all of the reducing radicals react with TiO_2 nanocrystallites to produce the stable $e_{TiO_2}^-$ radical (reactions 4−6)

$$e_{aq}^- + TiO_2 \rightarrow e_{TiO_2}^- \qquad (4)$$

$$H^\bullet + TiO_2 \rightarrow e_{TiO_2}^- \qquad (5)$$

$$(CH_3)_2C^\bullet OH + TiO_2 \rightarrow e_{TiO_2}^- \qquad (6)$$

Pulse Radiolysis Experiments. *Reaction of $e_{TiO_2}^-$ with H_2PtCl_6.* The reduction of H_2PtCl_6 by $e_{TiO_2}^-$ (reaction 7) was determined by pulse radiolysis of argon saturated solutions containing 0.2 M TiO_2 colloid of big particles, or 0.28 M TiO_2 colloid of small particles, in the presence of 0.2 M $(CH_3)_2CHOH$ at pH (2.9−3.0). H_2PtCl_6 concentrations were varied between $(0.4-1.25) \times 10^{-4}$ M

$$e_{TiO_2}^- + H_2PtCl_6 \rightarrow\rightarrow\rightarrow Pt^0 \qquad (7)$$

We were unable to separate the various reduction stages, although the final product is Pt^0. Under our experimental conditions, >95% of the hydrated electrons produced by the pulse reacted with the TiO_2 colloid to produce $e_{TiO_2}^-$, rather than with H_2PtCl_6. This is obvious when considering the rate constant of e_{aq}^- with TiO_2 (2.8×10^8 and 1.1×10^9 M^{-1} s^{-1} for the big and small particles, respectively),[14] compared to 2×10^{10} M^{-1} s^{-1} for the reaction of e_{aq}^- with H_2PtCl_6,[15] and taking into account the relative concentrations of TiO_2 and H_2PtCl_6. Similarly, $H^\bullet$ radicals will react mainly via reaction 3 rather than reactions 5 or 8: $k_3 = 7.5 \times 10^8$ M^{-1} s^{-1} [15] compared to

$$H^\bullet + H_2PtCl_6 \rightarrow\rightarrow\rightarrow H^+ + Pt^0 \qquad (8)$$

$k_5 = 10^6$ M^{-1} s^{-1} [14] and $k_8 = 7 \times 10^9$ M^{-1} s^{-1}.[15] $(CH_3)_2C^\bullet OH$ radical may react with H_2PtCl_6 in addition to the reaction with TiO_2 and might interfere with the kinetic measurements of reaction 7. It was observed that the initial absorption of $e_{TiO_2}^-$ at 600 nm decreased as the concentration of the chloroplatinic acid increased, from 0.022 in the absence of H_2PtCl_6 down to 0.01 at the highest concentration of the chloroplatinic acid used. This observation confirms the competition between TiO_2 and H_2PtCl_6 for the $(CH_3)_2C^\bullet OH$ radical. Nevertheless, in all the experiments carried out to determine k_7, a vertical increase of the absorptions was observed at 600 nm after the pulse, so that reactions 4−6 presenting the formation of $e_{TiO_2}^-$ were completely separated in time from the decay via reaction 7. The full decay of reaction 7 took place in the 10−40 ms time scale, whereas the formation of $e_{TiO_2}^-$ was completed within the sub ms time scale. A minor residual decay in the 1 to 2 s region was also observed. A typical example of the absorption decay at 600 nm is shown in Figure 1. Similar pulse experiments were

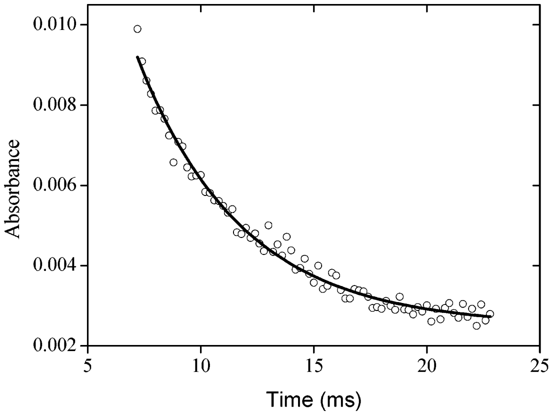

Figure 1. Decay of $e_{TiO_2}^-$ in the presence of H_2PtCl_6 Followed at 600 nm after pulse radiolysis of argon saturated solution containing 0.2 M TiO_2 (big particles), 9.5×10^{-5} M H_2PtCl_6, 0.2 M $(CH_3)_2CHOH$ at pH 3.0. The line represents first-order rate law.

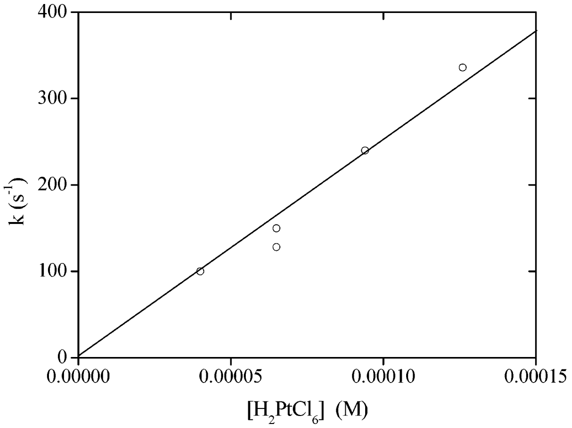

Figure 2. Pseudo first-order rate constant of reaction 7 as a function of $[H_2PtCl_6]$. 32 Gy per pulse, 0.2 M TiO_2 (big particles), 0.2 M 2-propanol at pH 3.0, Ar saturated Straight line corresponds to $k = 2.5 \times 10^6$ M^{-1} s^{-1}.

carried on with several chloroplatinic concentrations, showing linear dependence of the decay rate on $[H_2PtCl_6]$, yielding $k_7 = 2.5 \times 10^6$ M^{-1} s^{-1} for the big particles (Figure 2) and 6.1×10^6 M^{-1} s^{-1} for the small ones.

Comparison of Reactivity of Bare TiO_2 Colloid Particles with Pt Coated Particles. *Reaction of $e_{TiO_2}^-$ with Oxygen.* The reaction of $e_{TiO_2}^-$ with oxygen was measured in air saturated solutions at pH 3.2 and in the presence of 0.2 M 2-propanol. The decay of $e_{TiO_2}^-$ at 600 nm was followed after pulse irradiating solutions of TiO_2 coated with Pt^0 and compared to the decay of $e_{TiO_2}^-$ in the absence of Pt^0. The predominant part of the initial absorbance decays by a biexponential rate law, in the presence as well as in the absence of Pt^0 (reaction 9). Second-order rate constants of the fast and the slow decays (reaction 9f and 9s, respectively) have been measured at different concentrations of Pt^0 and compared to solutions without the platinum coating. The average results of 4−7 repetitive measurements at each concentration are summarized in Table 1, showing unequivocally that under our conditions, Pt^0 has no catalytic effect on the reduction of oxygen by $e_{TiO_2}^-$

$$e_{TiO_2}^- + O_2(+H^+) \rightarrow HO_2 + TiO_2 \tag{9}$$

An average value of the fast decay $k_9 = (1.9 \pm 0.6) \times 10^7$ M^{-1} s^{-1} is calculated.

Reaction of $e_{TiO_2}^-$ with H^+. The typical blue color of colloidal $e_{TiO_2}^-$ in acid solution is known to be stable under argon for many days. We observed that $e_{TiO_2}^-$, produced by a burst of 50 pulses, 30 Gy each on TiO_2 coated with Pt^0, disappears within several hours. Figure 3 presents a typical decay of $e_{TiO_2}^-$ produced in deaerated 0.2 M TiO_2 coated with 2×10^{-4} M Pt^0. The catalytic reaction obeys the same first order rate law throughout the decay process and reaches its end after practically all of the electrons (>90%) have been reacted, with no observable changes in the Pt^0.

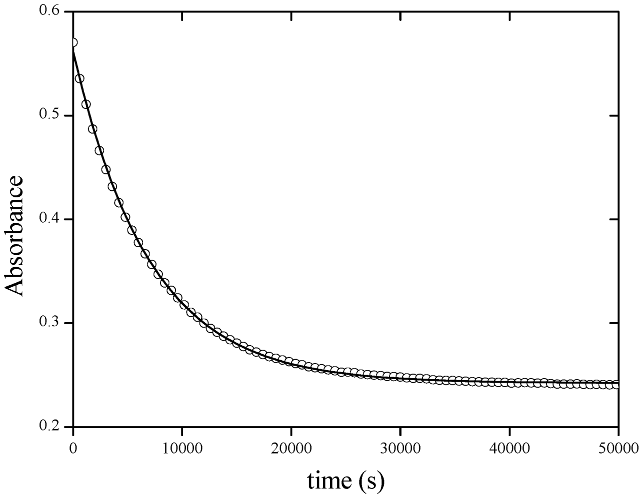

Figure 3. Decay of $e_{TiO_2}^-$ by reaction with H^+. Absorbance induced by 30 pulses (total 900 Gy) in 0.2 M TiO_2 saturated Ar, in the presence of 0.2 M 2-propanol at pH 2.4. Big TiO_2 particles coated with 2.5×10^{-4} M Pt^0.

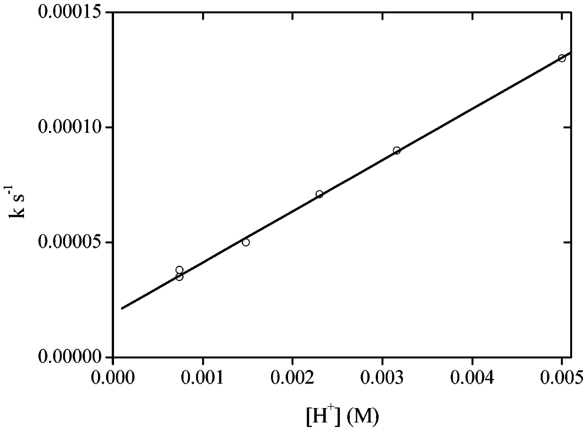

Figure 4. Catalyzed reaction of $e_{TiO_2}^-$ with H^+. Ar saturated solutions of TiO_2 coated with Pt^0. The rate Constant calculated from plots such as in Figure 3. $[TiO_2] = 0.2$ M, big particles, $[Pt^0] = 2 \times 10^{-4}$ M, [2-propanol] = 0.2 M.

TABLE 1: Reaction of $e_{TiO_2}^-$ with Oxygen in 0.2 M TiO_2 Coated with Different Concentrations of Pt^0 in Air Saturated Solutions ($O_2 = 2.4 \times 10^{-4}$ M) Containing 0.2 M $(CH_3)_2CHOH$ at pH 3.2

Pt^0 M	average k_{9s} M^{-1} s^{-1}	average k_{9f} M^{-1} s^{-1}
0	$(2.7 \pm 0.3) \times 10^4$	$(1.9 \pm 0.4) \times 10^7$
4.8×10^{-5}		$(2.0 \pm 0.6) \times 10^7$
1.1×10^{-4}		$(1.7 \pm 0.5) \times 10^7$
2.3×10^{-4}	$(2.1 \pm 0.7) \times 10^4$	$(1.9 \pm 0.7) \times 10^7$

At a given Pt^0 concentration, the decay rate of $e_{TiO_2}^-$ increased linearly with H^+ concentration. This is shown in Figure 4. The linear dependence suggests that hydrogen is produced by reductions of H^+ and to a lesser extent by reduction of H_2O. The reaction with H_2O is introduced in order to rationalize the intercept observed in Figure 4. The Pt^0 mediated reduction of

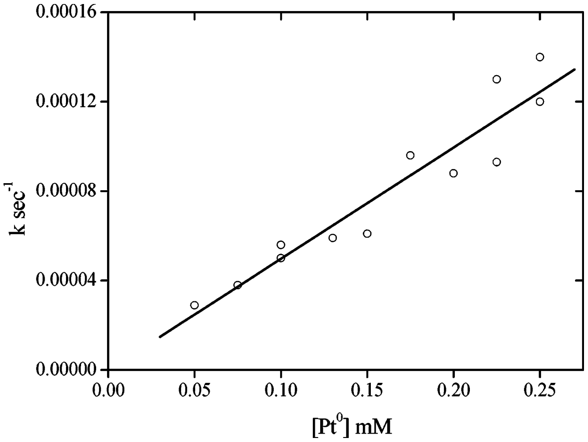

Figure 5. Catalyzed decay of $e_{TiO_2}^-$ as a function of Pt^0 catalyst concentration. Pt^0 coated on TiO_2 at pH 2.5. The rate constant taken from plots such as Figure 3, $[TiO_2] = 0.2$ M, big particles, [2-propanol] = 0.2 M, Ar saturated. The line corresponds to $k = 0.52\ M^{-1}\ s^{-1}$.

H^+ apparently involves adsorbed hydrogen atoms (reaction 10 and 11)

$$e_{TiO_2}^- + H^+(Pt^0) \rightarrow H^\bullet(Pt^0) + TiO_2 \qquad (10)$$

$$e_{TiO_2}^- + H_2O(Pt^0) \rightarrow H^\bullet(Pt^0) + TiO_2 + OH^- \qquad (11)$$

$$e_{TiO_2}^- + H^\bullet(Pt^0) + H^+ \rightarrow H_2 \qquad (12)$$

$$H^\bullet(Pt^0) + H^\bullet(Pt^0) \rightarrow H_2 \qquad (13)$$

It should be emphasize that the presence of Pt^0 is essential for reaction 10 and 11 to take place. The adsorbed hydrogen radicals from reaction 10 and 11 produce molecular hydrogen by reactions 12 and 13, rather than hydrogen abstraction from $(CH_3)_2CHOH$ (reaction 3). This will be further discussed later. Our results yield average values $k_{10} = 1.3 \times 10^2[Pt^0]\ M^{-1}\ s^{-1}$ and $k_{11} = 0.1[Pt^0]\ s^{-1}$.

Kinetic measurements at different platinum concentrations and at a given pH show that the rate of $e_{TiO_2}^-$ decay increases linearly with Pt^0 concentration. This is shown in Figure 5.

The linear increase is expected if the added Pt^0 increases the number of catalytic sites, which may be aggregates of Pt^0 settled on the TiO_2 surface or separate Pt^0 atoms. The possibility that increasing Pt^0 concentration enhances the catalysis by increasing the surface area of existing aggregates can be ruled out, as in such a case where the rate is expected to increase with the 2/3 power of the concentration rather than the observed linear dependency. This conclusion is also in agreement with an earlier observation that the Pt^0 aggregates grow up to a constant average size, which does not depend on the Pt^0 concentration.[11]

It is worthwhile to consider the distribution of $e_{TiO_2}^-$ and Pt^0 on the TiO_2 particles. The average number of TiO_2 molecules per particle in solutions of big particles (diameter 5 nm) is estimated as about 2000. This value is derived from the equation: $n = \pi d^3 \rho A/6m$, where n is the number of TiO_2 molecules in a particle, d is the particle diameter in cm, ρ is the density of TiO_2 taken as 4 g/cm^3, A stands for Avogadro's number, and m is the molecular weight of TiO_2. This calculation leads to a concentration of about 10^{-4} M of colloid particles in the 0.2 M TiO_2 solutions. Thus, the initial concentration of $e_{TiO_2}^-$ produced by the electron beam (about 10^{-3} M) corresponds to an average of 10 electrons per TiO_2 nanoparticle. The average number of Pt^0 atoms per TiO_2 nanoparticle is considerably smaller: The formal concentration of Pt^0 (Figure 5) is in the range $5 \times 10^{-5} - 2.5 \times 10^{-4}$ M, meaning that on the average each colloid particle is loaded with only 0−3 atoms of Pt^0 (depending on the Pt^0 concentration) and most TiO_2 surface is not covered with platinum. A significant fraction of the TiO_2 nanocrystallites has no Pt^0. If the decay of $e_{TiO_2}^-$ involves Pt^0 and electrons on the same nanocrystallite, only partial decay of $e_{TiO_2}^-$ is expected, contrary to the observation that the $e_{TiO_2}^-$ absorbance decays nearly to zero by a single-exponential process. Our observations can be rationalized by aggregation of the TiO_2 nano-particles as a three dimensional network,[16] which enables electron hopping between the nanocrystallites to Pt^0 sites. In addition, migration of Pt^0 through the aqueous suspension, in line with the Ostwald ripening, enables the Pt^0 catalyst activity at a number of TiO_2 aggregates.

GC Measurements. H_2 yields developed from reactions 1, 3, 12, and 13 have been determined after irradiating TiO_2 solutions in the presence as well as in the absence of platinum, at acid pH containing 0.2 M $(CH_3)_2CHOH$. Blank argon saturated aqueous solutions containing only $(CH_3)_2CHOH$ at the same pH were irradiated. In the blank solution, H_2 originates from three sources: (i) Reaction of e_{aq}^- ($G = 2.7$) with H^+ to give $H^\bullet$ followed by reaction 3; (ii) primary $H^\bullet$ atoms ($G = 0.6$) reacting according to (3); (iii) molecular yield of H_2 ($G = 0.45$). The total yield in the blank solution sums up to $G = 3.75$. The evolution of H_2 in TiO_2 solutions in the absence of platinum is expected to be lower: At the pH of the experiments (pH 2.7), there is competition between H^+ and TiO_2 for the e_{aq}^-. Taking the rate constant of e_{aq}^- with H^+ as $2.2 \times 10^{10}\ M^{-1}\ s^{-1}$ [15] and e_{aq}^- with TiO_2 as $2.6 \times 10^8\ M^{-1}\ s^{-1}$,[14] 50% of the solvated electrons react with H^+ to produce H_2 ($G = 1.3$). The rest of the solvated electrons produce $e_{TiO_2}^-$, which in the absence of Pt^0 do not produce H_2. Since practically all H atoms produce H_2 according to reaction 3, the calculated yield of H_2 is $1.3 + 0.45 + 0.6 = 2.35$. The experimental result from six different solutions showed an average yield of 2.4 ± 0.3, in very good agreement with the expected value.

When Pt^0 is also present, the H_2 yield is increased due to reactions 10−13. Furthermore, the $^\bullet OH$ radicals reacting with 2-propanol produce $(CH3)_2C^\bullet OH$ radicals, which eventually reduce TiO_2 to form $e_{TiO_2}^-$ according to reaction 6. This further increases the expected total H_2 yield. Had $e_{TiO_2}^-$ reacted with H^+/water producing free H atoms, the total molecular hydrogen yield would have increased to at least $3.75 + 2.7 = 6.45$. It should be noted that the expected yield in the case of hydrogen abstraction from the 2-propanol by the hydrogen atom intermediate must be even higher, because generation of free H atoms from $e_{TiO_2}^-$ would have initiated a chain reaction producing H_2. However, the energy of $e_{TiO_2}^-$ is not sufficient for generation of free hydrogen atoms, and consequently, adsorbed hydrogen atoms recombine on the surface of Pt^0 to produce molecular hydrogen (reaction 13). In such mechanism taking into consideration the competition between H^+ and TiO_2 for e_{aq}^-, a total hydrogen yield of 4.7 is predicted. The average of six different TiO_2/Pt^0 solutions at pH 2.3 showed a yield of (4.8 ± 0.6), in excellent agreement with the value predicted above on the basis of adsorbed hydrogen atom recombination.

Conclusions

The reaction of $e_{TiO_2}^-$ with water and hydrogen ions is easily separated in time from the generation of $e_{TiO_2}^-$ by pulse radiolysis. Thus, we have been able to study the kinetics of the electron decay as a function of pH. The pseudo-first-order kinetics and the first-order rate dependency on H^+ and Pt^0

concentrations show that the rate determining step of the catalytic reduction is the transfer of the TiO_2 excess electron from the Pt^0 cluster to H^+ and H_2O. The results enable the elucidation of the separate reaction rate constants for H^+ and water.

Pt^0 as well as other metals are well-known to enhance photocatalytic oxidations of organic solutes. Wang, Heller, and Gerischer[12] have shown that catalyzed oxygen reduction by surface Pd^0 increases photocatalytic oxidation yields by preventing accumulation of electrons on the TiO_2 particles, thus inhibiting the rate of electron−hole recombination. On the other hand, Bahnemann, Hilgendorff, and Memming[8] attributed the enhanced oxidation to the metal effect on increasing charge separation. The present work supports the latter conclusion, although the role of platinum may differ from that of palladium.

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