Kinetics of Hydrogen Production upon Reduction of Aqueous TiO_2 Nanoparticles Catalyzed by Pd^0, Pt^0, or Au^0 Coatings and an Unusual Hydrogen Abstraction; Steady State and Pulse Radiolysis Study

David Behar* and Joseph Rabani*

Department of Physical Chemistry and Accelerator Unit, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Reduction of H^+ by TiO_2 electrons ($e_{TiO_2}^-$) in aqueous colloidal solution takes place in the presence of surface metal catalysts. The catalytic reduction gives rise to adsorbed hydrogen atoms. In the presence of Pd^0 or Pt^0, material balance shows that most of the adsorbed H atoms combine to molecular hydrogen. When the TiO_2 nanoparticles are partially coated with Au^0 instead of Pd^0 or Pt^0, a higher than expected molecular hydrogen level is observed, attributed to a short chain reaction involving hydrogen abstraction from 2-propanol. This unusual hydrogen abstraction reaction has not been reported before. The mechanism and energy balance are discussed. The surface modification of TiO_2 nanoparticles was carried out by reduction of K_2PdCl_4, H_2PtCl_6, or $HAuCl_4$ with $e_{TiO_2}^-$. The latter had been generated through electron injection from hydrated electrons, hydrogen atoms, or 2-propanol radicals, produced by γ or pulse radiolysis prior to the addition of the metal compounds. Upon addition of the metal compounds, immediate reactions take place producing metals clusters (M^0) by multistep reductions reactions on the TiO_2 surface. The chemical kinetics involving the different metals and the reaction rate constant of e_{aq}^- and $e_{TiO_2}^-$ with $AuCl_4^-$ is also reported.

Introduction

Nobel metal particles deposited on nanocrystallite semiconductors have been used widely to enhance the photocatalytic efficiencies,[1−6] particularly Pt^0, Au^0, or Pd^0 on TiO_2. The noble metals act as an electron sink promoting interfacial charge-transfer processes in the composite systems.[7,8] Graetzel[9] has noted that free diffusion of charge carriers permits electron transfer within a time of 0.1 ps, thus competing effectively with electron−hole recombination. Wang, Heller, and Gerischer[10] have shown that catalyzed oxygen reduction by $e_{TiO_2}^-$ involving surface metal increases the photocatalytic oxidation yields by preventing accumulation of electrons on the TiO_2 particles, thus inhibiting the rate of electron−hole recombination. Subramanian et al.[11] observed a relationship between the photocatalytic activity of TiO_2 film doped with Au^0 nanoparticles and the effect of gold particle size on the Fermi level of the composite: A greater shift in the Fermi level toward more negative potentials was observed with smaller Au nanoparticles, causing greater photocatalytic reduction efficiency. It has been shown recently (in the ZnO/Pt nanocrystallites, which have energy properties similar to those of TiO_2/Pt), that excess electrons reside exclusively on the Pt^0.[12] Thus, it is not surprising that the TiO_2/Pt and similar systems show enhanced photocatalytic oxidation such as biphenol, ammonia, and CO compared to bare TiO_2.[13−16]

A number of works have been published concerning photochemical generation of hydrogen in a Pt^0 modified TiO_2 surface.[17,18] Bamwenda et al.[17] studied photocatalytic H_2 generation by Au/TiO_2 and Pt/TiO_2 in illuminated aqueous 5 M C_2H_5OH suspension and reported strong dependence of the catalytic activity on the preparation method. It has been reported that the overall activity of Au^0 was generally about 30% lower compared to Pt^0. The H_2 yield depended on the metal content, with a maximum in the range 0.3−1 wt % Pt^0. The yield was found to depend on initial pH (maximum at 4−7) and decreased considerably at highly acidic and highly basic suspensions.[17] Kanno et al.[19] reported that the catalytic activity of Pt/TiO_2 was three times higher than that of Au/TiO_2. Surface Pd^0 increased the quantum efficiency of the photooxidation of aqueous 2,2-dichloropropionate threefold at 0.01 wt % Pd compared to bare TiO_2.[10] Xu et al.[20] studied Pd sputtering on a TiO_2 surface at room temperature and observed competition between Pd^0 cluster growth and nucleation of new sites. Initially new seeds were formed, but with increasing the amount of deposition manyfold most of the Pd atoms accumulate at the initially produced seeds and only a small portion form new seeds. It was also found that Pd atoms tend to form dimers and tetramers. No isolated Pd atoms were ever observed, suggesting that the dimmer is the smallest stable nuclei.

Reduction reactions of excess electrons in TiO_2 nanocrystallites produced by pulse radiolysis have been studied earlier.[21] Reduction rates of several substrates were found to depend on TiO_2 particle size. Cu^{2+}, ClO_2^-, ClO_3^-, NO_2^-, and NO_3^- showed decay of the $e_{TiO_2}^-$ electron predominately by a single pseudo first-order process. Alternatively, hydrogen peroxide and oxygen show a multiexponential decay. In a recent publication[22] we studied the reactions of $e_{TiO_2}^-$ with H^+ and water in the TiO_2/Pt system and elucidated the reaction mechanism and radiation yields of H_2. The decay of the TiO_2 electron was found to be a single pseudo first-order process depending linearly on Pt^0 and H^+ concentrations. The energy of $e_{TiO_2}^-$ is not sufficient for generation of free hydrogen atoms, although adsorbed atoms on the Pt^0 surface are produced. These atoms eventually combine to molecular hydrogen. It has been shown that the energy of

* Corresponding authors. E-mail: behar@vms.huji.ac.il; rabani@vms.huji.ac.il.

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the adsorbed hydrogen atom on the Pt^0 surface is not sufficient to abstract hydrogen from 2-propanol. A similar observation was reported in Au/TiO_2 by Hussein and Rudham.[23]

The purpose of the present work is to expand the earlier work to additional metals, namely Pd^0 and Au^0, comparing their reactivity toward H^+ and H_2O reduction and their catalytic role in adsorbed hydrogen atom reaction.

Experimental Section

Colloidal TiO_2 solutions were prepared by hydrolysis of $TiCl_4$ (Aldrich 99.9%). As reported previously,[24] 25 mL of $TiCl_4$ was 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. Thirty minutes after the addition of the $TiCl_4$, the solution was dialyzed against HCl solution at pH 3 (pore size cutoff 6000−8000). The suspension was kept at 45 °C for several days to increase the size of the particles to an average diameter of about 5 nm. TiO_2 concentrations, in terms of molecules, were determined by spectrophotometric measurements at 215 nm using $\epsilon = 6050\ M^{-1}\ cm^{-1}$.

Radiolysis. A ^{137}Cs γ source of 9 Gy/min or a linear electron beam accelerator (Varian 7715) operated at 5 MeV and maximum current of 200 mA with 1.5 μs pulse duration were used as the radiation sources for production of excess electrons in the TiO_2 nanoparticles. At the highest electron beam intensity about 1.5×10^{-5} M reducing radicals were produced by a single pulse (taking $G_{e_{aq}^-} + G(OH^\bullet) + G(H^\bullet) = 6$, where G_x stands for the number of X molecules produced by 100 eV absorbed radiation). The absorbance changes of $e_{TiO_2}^-$ were monitored at 600 nm. The reactivity of Au^{3+}, Pd^{2+}, and Pt^{4+} toward the hydrated electron, e_{aq}^-, was studied by its decay kinetics using pulse radiolysis by competition with methyl viologen (MV^{2+}) applying 0.2 μs pulses, which yields about 1×10^{-6} M e_{aq}^- per pulse. The absorption changes of the methyl viologen radical were also followed at 600 nm.

TiO_2 Coatings with Pt, Au, and Pd. Deaerated (Ar bubbling) colloid solutions of TiO_2 (4−5 mL of 0.2M) containing (0.2−2) M 2-propanol, sealed in test tube by means of a rubber septum were irradiated by γ rays or electron beam. Under these conditions $e_{TiO_2}^-$ builds up; its concentration was adjusted to exceed by about 30% the equivalent concentration of the metal precursor (namely $[e_{TiO_2}^-] = 1.3 \times 2x[Pd(II)]$ or $1.3 \times 3x[Au(III)]$ or $1.3 \times 4x[Pt(IV)]$). In the absence of the metal salts $e_{TiO_2}^-$ is stable for weeks. Upon injection of the metal complexes, instantaneous reduction to the free metals is observed. The unreacted electrons remaining at the end of the reduction process were destroyed by saturating the solution with oxygen. Finally the oxygen was removed by saturating again with argon.

Kinetic Measurements. Pulse radiolysis experiments were carried out in a 2 cm quartz cell (6 cm light path) at (22 ± 2) °C. The pulse duration was 0.2−1.5 μs, yielding $(1-7) \times 10^{-6}$ M e_{aq}^-. 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 kinetics of e_{aq}^- reaction with methyl viologen and of $e_{TiO_2}^-$ reaction with the metal complexes was studied by the 600 nm absorbance changes. Rate constants of the reaction of e_{aq}^- with the metal complexes were determined by competition with methyl viologen. For kinetic measurement of $e_{TiO_2}^-$ reactions with H^+ and water, which endure several hours, solutions of TiO_2 colloid coated with the reduced metals were transferred into a quartz cell and bubbled with argon for at least 20 min. The 1 cm cell was subsequently irradiated by electron beam, receiving 30−40 consecutive pulses of about 30 Gy each within several seconds. The TiO_2 nanoparticles in the suspension become loaded with excess $e_{TiO_2}^-$. The cell was then transferred to a Hewlett-Packard diode array spectrophotometer at 25 °C for the kinetic measurements. The optical density was monitored against air without compensating for the cells reflection and absorbance, which in some cases, stable coloration of the quartz during irradiation took place.

Hydrogen Determination. Several (2−3) sealed test tubes containing Ar-saturated colloid solutions of TiO_2/M^0 in the presence of 2-propanol were irradiated in a ^{137}Cs γ source for 3 h, receiving a total dose of 1.6 kGy. The irradiation was carried out together with the same number of reference samples containing aqueous 2-propanol (0.2 M or 2 M) in the absence of TiO_2/M^0 at acid pH. The reference samples served to determine the hydrogen yields by comparison between the hydrogen signals in the reference and in the TiO_2/M^0 solutions. The test tubes were left at room temperature for 17−20 h to ensure completion of the reaction producing hydrogen. During measurements the test tubes were kept in a 25 °C thermostat. Given volumes from the gas phase, equilibrated by vigorous shaking of the samples were injected to the HP-5890 gas chromatograph (TCD detector, Porapak column from Supelco and argon as the gas carrier).

Results and Discussion

The primary radicals and molecules produced in water upon electron-beam or γ irradiation are shown in eq 1. The numbers in parentheses represent the respective *G* values. Where *G* stands for the number of radicals or molecules produced per 100 eV of absorbed radiation.

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

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.

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

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

In the absence of oxygen and the metal complexes the reducing radicals react with TiO_2 nanoparticles to produce the stable $e_{TiO_2}^-$ radical (reactions (4−6)).

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

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

$$(CH_3)_2C^\bullet OH + TiO_2 \rightarrow e_{TiO_2}^- + H^+ + (CH3)_2CO \quad (6)$$

Pulse Radiolysis Experiments. *Reaction of e_{aq}^- with the Noble Metal Complexes.* The reaction of hydrated electrons with $PtCl_6^{2-}$ and $PdCl_4^{2-}$ have been reported previously.[25] We have verified the above rate constants and determined the e_{aq}^- rate constants with $AuCl_4^-$ by competition of the metal complexes with methyl viologen. Ar-saturated 0.2 M *tert*-butyl alcohol solutions containing 2×10^{-5} M methyl viologen at pH 5.5 were exposed to pulses of 0.2 μs duration (1×10^{-6} M e_{aq}^-). The *tert*-butyl alcohol was chosen to scavenge the $OH^\bullet$ radicals (reaction 7) because its relatively inert radical intermediate cannot interfere with the studied competition reactions. Under

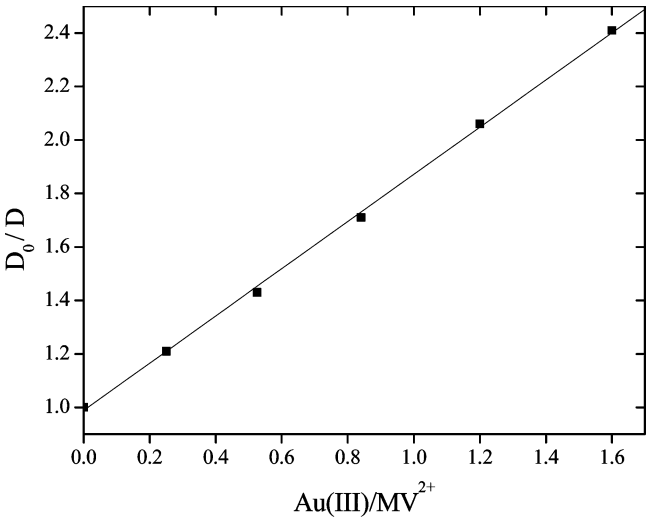

Figure 1. Competition of $AuCl_4^-$ and MV^{2+} for e_{aq}^- $[MV^{2+}] = 2 \times 10^{-5}$ M, 3 mM buffer acetate pH 5.5, Ar-saturated, 0.2 M *tert*-butyl alcohol, 0.2 μs pulse (1 μM e_{aq}^-). Absorption of $MV^{\bullet+}$ was followed at 600 nm.

the conditions of this work, at pH 5.5 about 6.5% of the reducing radicals are in the form of H atoms and the rest 93.5% are solvated electrons, e_{aq}^-. Reactions of hydrogen atoms are shared between *tert*-butyl alcohol, MV^{2+}, and the respective metal complexes; therefore, the relative concentration of the H atoms is small and does not interfere with the competition reactions measured here. The hydrated electron, e_{aq}^-, reduces methyl viologen according to reaction 8 with an average rate constant $k_8 = 6.9 \times 10^{10}$ $M^{-1}sec^{-1}$.[25]

$$OH + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O \quad (7)$$

$$e_{aq}^- + MV^{2+} \rightarrow MV^{+\bullet} \quad (8)$$

$$e_{aq}^- + MCl_x^{y-} \rightarrow \rightarrow \rightarrow M^0 + XCl^- \quad (9)$$

$$e_{aq}^- + Au(III) \rightarrow \rightarrow \rightarrow Au^0 \quad (10)$$

The expression describing the competition reactions of a metal complex and MV^{2+} (reaction 8 and 9) is $D_0/D = k_9[MCl_x^{y-}]/k_8[MV^{2+}] + 1$, where D_0 is the maximum optical density of the $MV^{\bullet+}$ radical in the absence of MCl_x^{y-} and D is the maximum optical density of $MV^{\bullet+}$ in the presence of MCl_x^{y-}. From plots of D_0/D versus $[Pd(II)]/[MV^{2+}]$ and $Pt(IV)/MV^{2+}$ (not given here) we obtained $k_{9Pd} = 1.2 \times 10^{10}$ and $k_{9Pt} = 1.9 \times 10^{10}$ $M^{-1}s^{-1}$ in very good agreement with the value published previously.[25] Figure 1 presents the competition plot for Au(III) from which a rate constant $k_{10} = 6.1 \times 10^{10}$ $M^{-1}s^{-1}$ is derived. This rate constant presumably presents the first reduction step of the multicharged Au complex. It should be noted that depending on conditions, the formation of $MV^{\bullet+}$ in the presence of the metal complexes is followed by partial decay. As a result, partial decay of absorbance is observed, which is considerably slower than the build up. Corrections have been made for the relatively small contribution of this decay to the observed rate.

Reaction of $e_{TiO_2}^-$ with $AuCl_4^-$. The reduction of $AuCl_4^-$ by $e_{TiO_2}^-$ (reaction 11) was studied by pulse radiolysis of deaerated solutions containing 0.2 M TiO_2 colloid in the presence of 0.5 M $(CH_3)_3COH$ at pH 2.6 and 1.5 μs pulse producing about 6×10^{-6} molar e_{aq}^-. Under these conditions most of the primary reducing radicals produced by the pulse react with the TiO_2 to

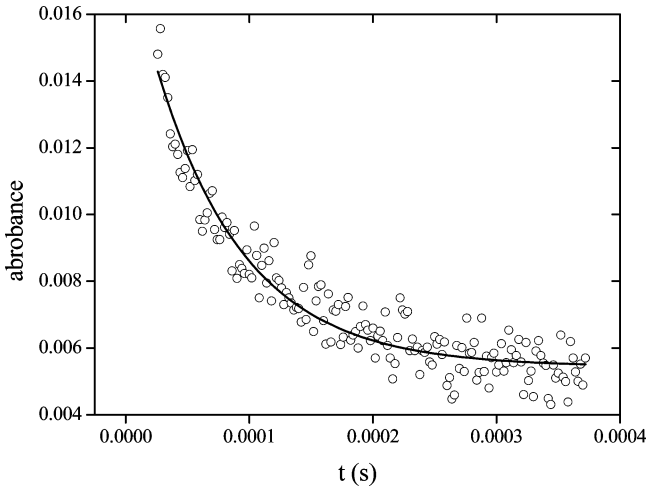

Figure 2. Decay of $e_{TiO_2}^-$ absorbance at 600 nm in the presence of $HAuCl_4$ after pulse radiolysis of argon-saturated solution containing 0.2 M TiO_2, 6.3×10^{-6} M $HAuCl_4$, 0.5 M $(CH_3)_3COH$ at pH 2.6. The line represents first-order rate law.

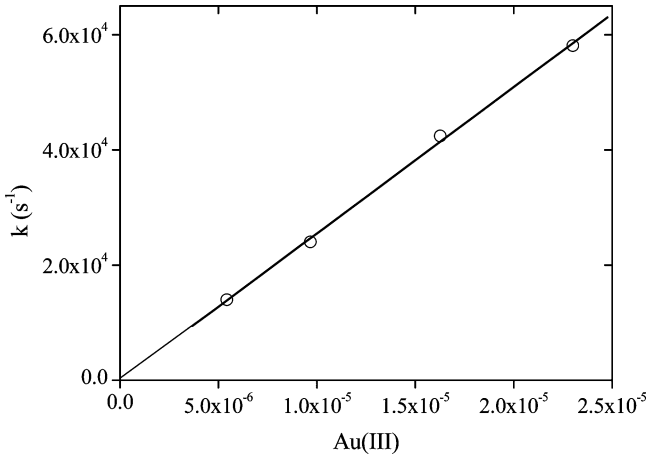

Figure 3. Pseudo first-order rate constant of reaction 11 as a function of $[HAuCl_4]$, 0.2 M TiO_2, 0.5 M *tert*-butyl alcohol at pH 2.6, Ar-saturated.

form $e_{TiO_2}^-$. About 4−10% of these radicals may react with the gold complex,[25] depending on the gold concentration and competing with the studied reaction 11. Note that reaction 11 does not produce metallic gold directly, but the one and two electrons reduced metal complex intermediates disproportionate and regenerate in part the $AuCl_4^-$.

$$e_{TiO_2}^- + Au(III) \rightarrow \rightarrow \rightarrow Au^0 \quad (11)$$

A typical example of the $e_{TiO_2}^-$ absorption decay at 600 nm is shown in Figure 2. The pseudo first-order rate constants for $e_{TiO_2}^-$ decay plotted versus $AuCl_4^-$ concentration is given in Figure 3, from which $k_{11} = 2.5 \times 10^9$ $M^{-1}s^{-1}$ is derived. In this plot the concentrations of $AuCl_4^-$ have been corrected for the average depletion during reaction.

It should be noted that the rate constant derived here is about 3 orders of magnitude larger than the value of 2.5×10^6 measured for the parallel reaction of $e_{TiO_2}^-$ with H_2PtCl_6.[22]

Reduction of H^+ by $e_{TiO_2}^-$ in the Presence of TiO_2 Doped with Pd^0, Pt^0, and Au^0. In a previous work[22] we showed that the typical blue color of colloidal $e_{TiO_2}^-$ in acid solution, which is stable under argon for many days, disappears within several

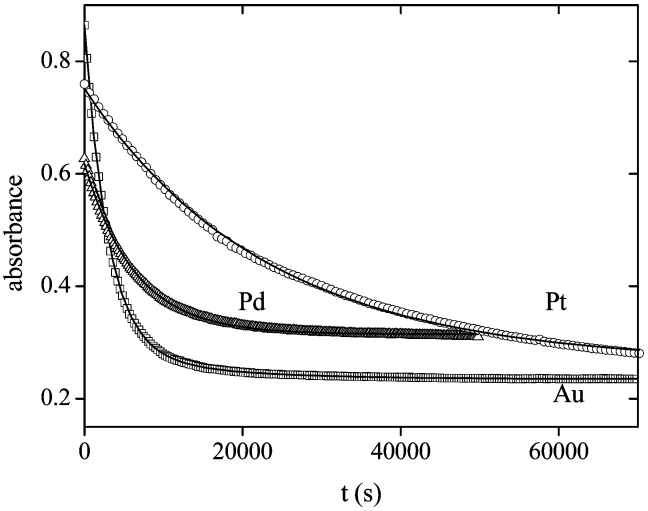

Figure 4. Effect of metal coatings on the rate of reaction 12. Absorbance induced by 30−40 pulses (total 900−1200 Gy) in 0.2 M TiO_2 Ar-saturated, in the presence of 0.2 M 2-propanol at pH 2.9. TiO_2 particles coated with $(1.3 \pm 0.1) \times 10^{-4}$M Au^0, Pd^0 or Pt^0. The solid lines represent first-order fits with the calculated pseudo rate constants, $k_{Au} = 3.4 \times 10^{-4}s^{-1}$, $k_{Pd} = 1.8 \times 10^{-4}s^{-1}$, and $k_{Pt} = 4.4 \times 10^{-5}s^{-1}$.

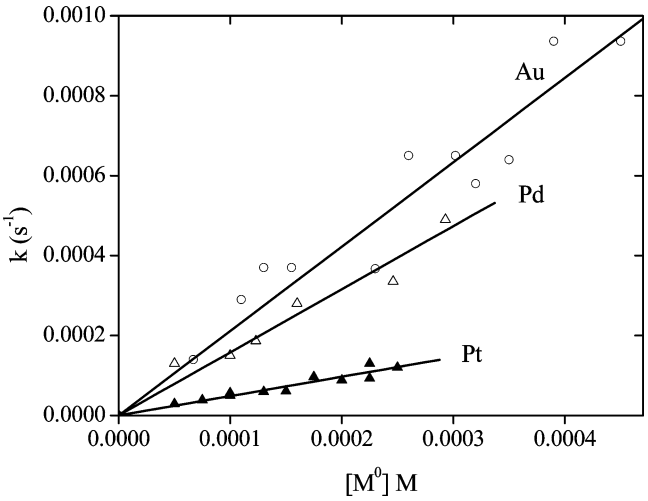

Figure 5. Effect of coating metal concentrations on the rate of reaction 12. The pseudo rate constants were taken from plots such as in Figure 4. 0.2 M TiO_2, 0.2 M 2-propanol at pH 2.6, Ar-saturated. The slopes of the straight lines correspond to $k_{Pt} = 0.48 \pm 0.02$, $k_{Pd} = 1.58 \pm 0.04$, and $k_{Au} = 2.1 \pm 0.1$ s^{-1}.

hours when the TiO_2 is coated with Pt^0 due to the reaction of $e_{TiO_2}^-$ with H^+ and H_2O.

$$e_{TiO_2}^- + H^+(M^0) \rightarrow H^\bullet(M^0) + TiO_2 \quad (12)$$

$$e_{TiO_2}^- + H_2O(M^0) \rightarrow H^\bullet(M^0) + TiO_2 + OH- \quad (13)$$

In the present work the decay kinetics of $e_{TiO_2}^-$ in TiO_2 coated with three different metals, Pt^0, Pd^0, and Au^0, is compared (Figure 4). All three cases obey first-order rate law.

Kinetic measurements at different metal concentrations show linear dependency of $e_{TiO_2}^-$ decay rate with M^0 concentration (Figure 5), resulting from increasing the number of active sites rather than the surface area of the adsorbed metals. In the latter case, $^2/_3$ power dependence on the metal concentration would be observed instead of the linear dependence. In contrast with the linear dependence reported here, Xu et al.[20] observed that increasing the amount of palladium deposition predominantly

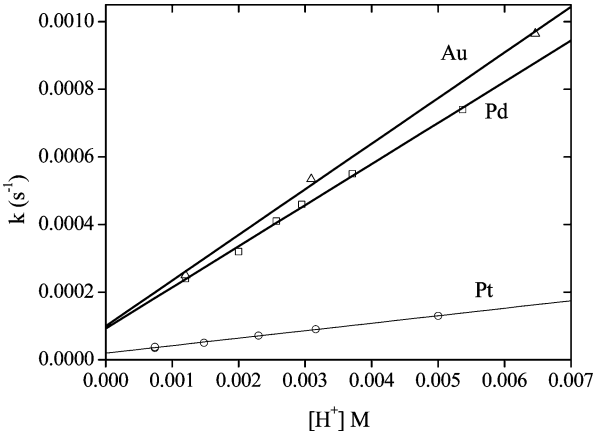

Figure 6. Effect of H^+ concentration on the rate of reaction 12. Ar-saturated solutions of TiO_2 coated with 2×10^{-4} M Pd^0, Au^0, or Pt^0. The rate constant calculated from plots such as in Figure 4. $[TiO_2] =$ 0.2 M, 0.2 M 2-propanol. The slopes of the straight lines represent the pseudo first-order rate constant for reduction of H^+: $k_{Pt}(H^+) = 0.022 \pm 0.004$, $k_{Pd}(H^+) = 0.12 \pm 0.01$, and $k_{Au}(H^+) = 0.14 \pm 0.01$ s^{-1}. The intercepts represent the pseudo first-order rate constant of water reduction: $(2.0 \pm 0.2) \times 10^{-5}$, $(9 \pm 1) \times 10^{-5}$ and $(1.0 \pm 0.2) \times 10^{-4}s^{-1}$, respectively.

induces growth of the initially formed seeds, and only a small portion of the metal form new seeds. This contradiction is attributed to different preparation methods of the clusters. Although Xu et al.[20] used sputtering of the Pd metal on TiO_2 surfaces, in the present work $e_{TiO_2}^-$ radicals were distributed randomly on the TiO_2 colloid particles before injecting the metal complex.

At a given metal M^0 concentration the decay rate of $e_{TiO_2}^-$ increased linearly with H^+ concentration for all metals tested as shown in Figure 6. This dependence means that hydrogen is produced predominantly by reaction 12 and to a much lesser extent by reaction 13 as can be concluded from the relatively small intercepts in Figure 6.

The adsorbed hydrogen radicals from reactions 12 and 13 produce molecular hydrogen by reactions 14 and 15. However, gold also catalyzes the reaction of $H^\bullet(M^0)$ with 2-propanol; this will be discussed later.

$$e_{TiO_2}^- + H^\bullet(M^0) + H^+ \rightarrow H_2 \quad (14)$$

$$H^\bullet(M^0) + H^\bullet(M^0) \rightarrow H_2 \quad (15)$$

Third-order rate constants for reaction 12, calculated from Figure 6 for the three metals are $k_{Pt} = 1 \times 10^2[Pt^0]$ $M^{-1}s^{-1}$, $k_{Pd} = 6 \times 10^2[Pd^0]$ $M^{-1}s^{-1}$, and $k_{Au} = 7 \times 10^2[Au^0]$ $M^{-1}s^{-1}$. These values are in fair agreement with those calculated from the results of Figure 5.

The TiO_2 used here has an average diameter of 5 nm and an average of 2000 TiO_2 molecules per particle. At the lowest $[M^0]$, the TiO_2 concentration in terms of colloid particles (each containing an average of 2000 TiO_2 molecules) is comparable to the atomic concentrations of the metals. Because the metal atoms tend to aggregate,[22] most TiO_2 nanoparticles are not expected to have metal deposit. However, under our conditions $e_{TiO_2}^-$ builds up to a level of 10 excess electrons per TiO_2 particle. Under such conditions, if M^0 interacts only with $e_{TiO_2}^-$ on the same nanoparticles, then a partial decay of these electrons is expected. This is in contradiction to the observed single-exponential decay accounting for most $e_{TiO_2}^-$ absorbance. The results indicate that $e_{TiO_2}^-$ produced on metal-free TiO_2 nanocrystallites decays by interparticle reaction involving metal

TABLE 1: Comparison of Hydrogen Yields of Different Doped Metals on TiO_2

metal	pH	$G(H_2)$ $[M^0]$0.1 mM	$G(H_2)$ $[M^0]$0.2 mM	$G(H_2)$ $[M^0]$0.2 mM
		0.2 M 2-PrOH		2 M 2-PrOH
	2.6	2.4	2.38	2.4
Pd	2.6	4.5	*	4.3
Pt	2.6	4.8	4.75	4.8
Au	2.6	5.3	5.4	6.65

*Partial coagulation appeared before the GC measurement.

loaded nanocrystallites. Alternatively, the catalyst M^0 may migrate from one nanocrystallite to another through the aqueous suspension between nanoparticles. Both colloid collision rate and equilibration between metal atoms in the bulk with metal aggregates on the TiO_2 nanosurfaces are much faster than the hour-long reduction of H^+ to molecular hydrogen.

GC measurements. Yields of molecular hydrogen produced by reactions 1, 3, 14, and 15 have been determined after irradiating TiO_2 solutions in the presence as well as in the absence of the reduced metals. Measurements were carried out in argon-saturated 0.2−2 M $(CH_3)_2CHOH$ at pH 2.6. Argon-saturated solutions containing only $(CH_3)_2CHOH$ were used as a reference. In the reference solution the H_2 originates from three sources: (i) Reaction of e_{aq}^- ($G = 2.7$) with H^+ producing $H^\bullet$ and subsequent dehydrogenation according to 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 sums up to $G = 3.75$. The evolution of H_2 in TiO_2 solutions in the absence of the reduced metals is expected to be lower because of competition between H^+ and TiO_2 for the e_{aq}^-. Taking the rate constant of e_{aq}^- with H^+ as 2.2×10^{10} $M^{-1}s^{-1}$ [25] and e_{aq}^- with TiO_2 as 2.6×10^8 $M^{-1}s^{-1}$,[24] 51% of the solvated electrons react with H^+ at pH 2.6 to produce H_2 ($G = 1.4$). The rest of the solvated electrons produce $e_{TiO_2}^-$, which in the absence of M^0 do not produce H_2. Because under these conditions practically all H atoms produce H_2 according to reaction 3, the calculated yield of H_2 is $1.4 + 0.45 + 0.6 = 2.45$. The average result from a large number of solutions is $G = 2.4 \pm 0.3$, in very good agreement with the calculated value. When M^0 is also present, the H_2 yield is expected to increase to 5.4 (an erroneous value of 4.7 was reported previously)[22] due to reactions (12−15). In fact, the hydrogen yield in the Pt^0 and Pd^0 systems is somewhat lower (Table 1). Presumably about 25% of the $e_{TiO_2}^-$ does not contribute to the formation of molecular hydrogen. This observation may be associated with trapped electrons, the reactions of which are too slow to be detected within the time of the measurements. Au^0 induces the formation of higher yields compared to Pt^0 and Pd^0. Thus, with Au^0/TiO_2 in 0.2 M 2-propanol the molecular hydrogen yield is 5.4, increasing to 6.65 at 2 M 2-propanol (Table 1). The effect of 2-propanol concentration is unique to the gold and is not observed in the other metal systems. The increased yield above $G(H_2) = 5.4$ is attributed to hydrogen abstraction from 2-propanol by $H^\bullet(Au^0)$, according to reaction 16.

$$H^\bullet(Au^0) + CH_3CHOHCH_3 \rightarrow Au^0 + H_2 + CH_3C^\bullet OHCH_3 \quad (16)$$

This abstraction induces a chain reaction because the 2-propanol radical produced by the hydrogen abstraction reacts with the nanoparticles according to reaction 6, thus regenerating the TiO_2 electron. The fact that $G(H_2)$ is only moderately increased compared to the Pt^0 and Pd^0 systems implies a relatively short chain, apparently due to the slowness of the hydrogen abstraction reaction, which has to compete with reaction 15. The value $G(H_2) = 5.4$ in 0.2 M 2-propanol is determined by two opposite effects: The relatively slow trapped $e_{TiO_2}^-$ reaction discussed above, which decreases the observed hydrogen yield within the time of the measurement, and the above chain reaction.

Energy Balance. At pH 2.6 the redox potential of the titanium dioxide conduction band electrons is $\epsilon(TiO_2/e_{TiO_2}^-) = -0.12 - 0.059$ pH $= -0.273$ V,[26] compared to -1.39 V for the $CH_3C^\bullet OHCH_3$ free radical.[27] Although the metal layer may induce a negative shift,[28] in view of the large difference, conversion of $e_{TiO_2}^-$ to $CH_3C^\bullet OHCH_3$ is thermodynamically not feasible, unless simultaneous electron injection from the 2-propanol radical to the gold-coated TiO_2 (reaction 6) takes place. The net result of reactions 12, 16, and 6 is the material balance eq 17, the standard free energy of which is -6.11 kcal[29] corresponding to $\epsilon = 0.1325 - 0.059$ pH $= -0.0217$ V at pH 2.6. Thus, under the conditions of the above hypothesis the chain reaction sequence becomes thermodynamically feasible, provided that the energy of the surface TiO_2 electron and $H^\bullet(M^0)$ does not differ much from that of the conduction band electron.

$$CH_3CHOHCH_3 \rightarrow H_2 + CH_3COCH_3 \quad (17)$$

Note that although the rate constant of reaction 6 is considerably lower than the diffusion-controlled limit,[21] the $CH_3C^\bullet OHCH_3$ radical is produced at the gold surface and is possibly linked to it. In such a case, nearly simultaneous reactions 16 and 6 become possible. The above suggestions are evidently speculative; however, we were unable to advance an alternative mechanism for the unexpectedly higher hydrogen yields in the gold system. The proposed chain reaction is in contradiction with Hussein and Rudham[23] who reported that Au/TiO_2 exhibit no activity for the photochemical dehydrogenation of 2-propanol. Our results on the hydrogen yields in the Au/TiO_2 system, compared to Pt/TiO_2 as given in the table are in discrepancy with the results of Bamwenda.[17] In our work part of the total hydrogen yield ($0.45 + 1.35 + 0.6 = 2.4$) originates from the radiation products that do not involve $e_{TiO_2}^-$; the rest of the measured yield, which originates from TiO_2 electrons, show the superiority of the gold over the platinum as catalyst in the H_2 production. This result is compared to the results of Bamwenda[17] where the $e_{TiO_2}^-$ originates from photolysis of TiO_2 suspensions doped with Au^0 and Pt^0. The trend in the efficiencies of these two metals in our work is the opposite of their findings where the yield of H_2 production was about 30% lower than that obtained with Pt^0. We do not have an explanation to this discrepancy. It may be possible that the discrepancy results from different properties of the doped TiO_2 particles because of different preparation procedures.

Conclusions

TiO_2 electrons were produced by electron injection of e_{aq}^- and 2-propanol radicals via radiolysis of acid aqueous TiO_2 colloidal solutions. The $e_{TiO_2}^-$ decays within several hours when the TiO_2 nanoparticles were coated with Pd^0, Pt^0, or Au^0. This decay is a result of catalyzed reaction between the $e_{TiO_2}^-$ and H^+ to form H_2. The rate of decay is third order for all three metal systems, namely, first order in $e_{TiO_2}^-$, H^+, and M^0 concentrations. The decay rate of $e_{TiO_2}^-$ either as a function of $[H^+]$ at constant $[M^0]$ or as function of $[M^0]$ at constant $[H^+]$ is in the order $Au^0/TiO_2 > Pd^0/TiO_2 > Pt^0/TiO_2$. The catalytic reduction gives rise to adsorbed hydrogen atoms, which combine to molecular hydrogen. Comparison of the measured H_2, produced upon irradiation, to the theoretical expected yield,

shows that about 25% of $e_{TiO_2}^-$ are trapped and do not contribute to molecular hydrogen during the time of the measurement. The catalytic efficiency of the doped metals is in the order $Au^0/TiO_2 > Pt^0/TiO_2 \geq Pd^0/TiO_2$, with Pt^0 and Pd^0 having almost the same yield with a difference that is in the range of the measurement accuracy. The Au^0/TiO_2 has a higher yield attributed to a short chain reaction involving hydrogen abstraction from 2-propanol by the adsorbed H atom, followed by electron injection to the TiO_2/Au particle from the adsorbed 2-propanol radical.

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References and Notes

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