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Light-Induced Reduction of Rhodium(III) and Palladium(II) on Titanium Dioxide Dispersions and the Selective Photochemical Separation and Recovery of Gold(III), Platinum(IV), and Rhodium(III) in Chloride Media

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Irradiation of aqueous TiO_2 dispersions containing palladium(II) or rhodium(III) chloride salts with AM1 simulated sunlight leads to the photoreduction of these metals, which are deposited on the semiconductor particle surface. Oxygen is detrimental to the photoreduction of rhodium(III) but not to the photoreduction of palladium(II). However, in both cases the reduction process is most efficient if the solution contains CH_3OH, which acts to scavenge valence band holes of the illuminated TiO_2 semiconductor. The selective photoreduction and recovery of precious metals from a dilute solution (as might be found in industrial wastes) have been investigated for a mixture of gold(III), platinum(IV), and rhodium(III) chloride salts as a function of various parameters (pH, presence or absence of O_2, presence or absence of a hole scavenger, and the concentration of the semiconductor). At pH 0, gold is easily separated from platinum and rhodium. The rate of photoreduction of gold(III) on TiO_2 is nearly independent of the concentration of the semiconductor, under the experimental conditions employed; the limiting rate is 2.7×10^{-7} M s^{-1}. The potential utility of this selective photochemical technique is discussed.

Introduction

Semiconductor materials (TiO_2, ZnO, CdS, and WO_3) have been shown to be excellent light mediators in the production of chemical fuels and in the photochemical degradation of several environmental contaminants.[2] Bandgap irradiation of the semiconductor particles generates electron/hole pairs that can be exploited in various redox processes. A most recent exploitation of the properties of these materials has considered the photochemical reduction of metals (especially noble metals).[3] The impetus of the present study finds justification in the variety of applications of semiconductors: preparation of photocatalysts, photoimaging processes, mechanistic studies, metal recovery, and selectivity in organic syntheses among others.[3] An especially useful application of the photoreduction process is in the selective recovery of such metals as gold, platinum, palladium, rhodium, and silver, as well as other coinage metals from industrial wastes. The photoreduced metal that gets deposited on the semiconductor particles can easily be separated from the slurry by centrifugation, followed by dissolution of the metal in HCl/HNO_3 mixtures. This has led to the facile recovery of the metal from the semiconductor TiO_2; the latter is chemically stable in aqua regia.[3q] We have explored this possibility earlier and we achieved the selective recovery of Au from a mixture of Au, Cu, Zn, and Ni via reduction on illuminated TiO_2.[3q] An advantage of using TiO_2 is its photochemical stability, its commercial availability, and its relatively low cost.[4]

Table I. Adsorption of Rhodium(III) (ppm) in Argon-Purged Solutions (25 mL) on TiO_2 (50 mg) Particles in the Dark

Rh (time 0)	Rh (in soln after 2-h stirring)	Rh (adsorbed)	pH
52.0	50.2	1.8	0
55.0	41.0	14.0	3.23
56.1	21.8	34.0	5.16
48.5	4.5	44.0	6.74

Herein, we report the results of the photochemical reduction of rhodium(III) and palladium(II) on TiO_2. More important, we demonstrate the selective photochemical separation and recovery of noble metals when present together in a dilute solution as may occur in a sample from industrial wastes. In particular, we show how gold, rhodium, and platinum can be separated selectively by photoreduction on the TiO_2 semiconductor material.

Experimental Section

TiO_2, Degussa P25 (anatase), was a generous gift of Degussa Canada Ltd. All chemicals were at least analytical grade and were employed as received. Stock solutions of $AuCl_3{\cdot}nH_2O$ (Johnson Matthey), H_2PtCl_6 (Fisher Scientific), $PdCl_2$ (Sigma), and $RhCl_3{\cdot}3H_2O$ (Fisher Scientific) were prepared fresh when needed by dissolving the calculated amount of the metal salt in water. Typically, the stock solutions contained 200–300 ppm of the metal (depending on the metal). The solutions were kept and handled in the dark to prevent any photochemical ligand exchange, as recently reported for H_2PtCl_6 solutions.[3d] Water was deionized and doubly distilled.

Unless otherwise noted, experiments were carried out in a 100-mL flask, closed with a rubber septum and an aluminum seal; 50 mL of solution was used and the concentration of TiO_2 was generally 2 g/L. Good stirring was provided to ensure uniform mixing of the suspension.

Irradiation was performed by using a Solarbox (CO.FO.MEGRA., Milano, Italy) that provided AM1 simulated sunlight at wavelengths >310 nm (1500-W xenon lamp with appropriate filters supplied by the manufacturer). The temperature inside the flask was 35 °C. When necessary, the suspension was purged with argon for ~15 min prior to illumination. Depending on the rate of reduction of the metal, 5-mL aliquots were taken every 2–5 min, and were subsequently analyzed for the metal (Pd or Rh) or for the metals (Au, Pt, Rh) when a mixture was employed. Metal analysis was carried out on a Perkin-Elmer 503 atomic absorption spectrophotometer equipped with a hollow-cathode single-element lamp. Oxygen was sampled from the gas phase and analyzed

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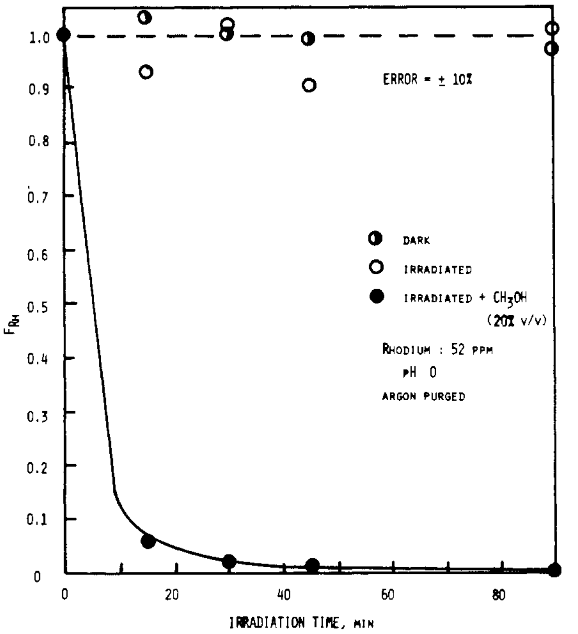

Figure 1. Photochemical reduction of Rh(III) (52 ppm) on TiO_2 (2 g/L) described by the fraction of metal remaining in solution as a function of irradiation time. Key: (◐) dark; (○) AM1 simulated-sunlight illumination; (●) illumination with 20% v/v methanol present. Conditions 25-mL argon-purged solutions; pH 0.

Table II. Determination of Rh(III) (ppm) Remaining in Argon-Purged Solution (25 mL) after 2-h Stirring in the Presence of TiO_2 (50 mg) in the Dark, under AM1 Simulated-Sunlight Illumination, and under Illumination with Methanol Present

Rh (time 0)	Rh (dark)	Rh ($h\nu$)	Rh ($h\nu$ + CH_3OH)	pH
52.0	50.2	52.7	0	0
55.0	41.0	49.6	3.0	3.23
56.1	21.8	31.7	1.5	5.16
48.5	4.5	21.0	1.9	6.74

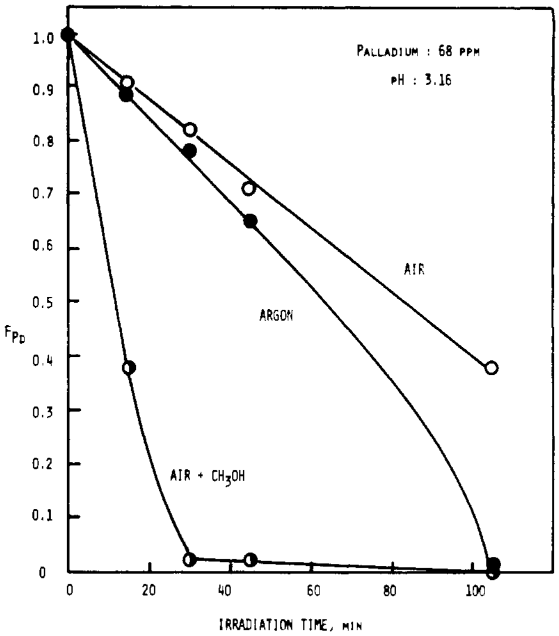

Figure 2. Fraction of Pd(II) remaining in solution as a function of irradiation time in the photochemical reduction of Pd(II) (68 ppm) in TiO_2 dispersions (2 g/L). Key: (●) argon-purged solutions; (○) air-equilibrated solutions; (◐) air-equilibrated solutions containing 10% v/v methanol. Conditions: pH 3.16; AM1 simulated sunlight.

Table III. Determination of Pd(II) (ppm) in Solution (50 mL) after 45-min Stirring in the Presence of 100 mg of TiO_2 under AM1 Simulated-Sunlight Illumination[a]

Pd(II) (time 0)	Pd(II) (argon)	Pd(II) (air)	Pd(II) (air + methanol)	pH
73	69	71	69	0
61	45	48	1	3.16
72	7	45	12	5.13

[a] Conditions: argon-purged solutions; air-equilibrated solutions; air-equilibrated solutions containing 10% v/v methanol.

by gas chromatographic techniques with a Gow-Mac gas chromatograph fitted with a molecular sieve 5A column and a thermoconductivity detector; argon was the carrier gas.

Results

(a) Photochemical Reduction of Rhodium(III) on TiO_2. Figure 1 illustrates the data on the photochemical reduction of rhodium(III) (52 ppm) on TiO_2 (50 mg) for 25-mL solutions containing 10% HCl (pH 0). Complete reduction of rhodium(III) in oxygen-free solutions occurs within 45 min of irradiation in the presence of CH_3OH (20% v/v) as the valence band hole (h_{vb}^+) scavenger.[3q] In acidic media, the reduction of O_2 by the conduction band electrons (e_{cb}^-) of TiO_2 is a thermodynamically favorable process that interferes with the reduction of rhodium(III). This contrasts with the photoreduction of gold(III) on TiO_2, where the presence of O_2 is inconsequential.[3q] No light-induced reduction of rhodium(III) occurs in the absence of methanol at pH 0, similar to our earlier findings on the photoreduction of gold(III) under identical experimental conditions.[3q] In addition, the results of Figure 1 show that in the dark no reduction occurs even in the presence of methanol. This confirms the reduction as a light-driven phenomenon.

The results of the interaction between $RhCl_3 \cdot 3H_2O$ and TiO_2 at various pHs in the dark are summarized in Table I. These data are crucial in the development of a procedure of metal separation by photochemical selective deposition, since adsorption phenomena and precipitation in the dark must be accounted for. The quantity of rhodium(III) removed from solution in the presence of TiO_2 increases with increasing pH. Two factors help explain this result: (i) the mechanism of adsorption of rhodium(III) onto the TiO_2 particle surface is analogous to that for adsorption of gold(III)[3q]—namely, Coulombic attraction between a cation and the negatively charged particle surface of TiO_2 (isoelectric point = 5.5); (ii) slow hydrolysis might occur to give $Rh(OH)_3 \cdot nH_2O$ or $Rh_2O_3 \cdot nH_2O$.[5,6]

In Table II, we compare the quantity of rhodium(III) remaining in solution at various pHs in the presence of TiO_2 under dark conditions, under simulated sunlight illumination, and under illumination where the solution also contains CH_3OH. The solutions were argon-purged to avoid interference from oxygen. It is clear that in very acidic media (pH 0) photoreduction occurs in the methanolic media with TiO_2 present. This is also confirmed by a change in color of the slurry from white to dark gray (rhodium(0) on TiO_2). Of importance is the observation that in the dark and at pH 6.74, nearly 90% of the rhodium(III) is adsorbed on the semiconductor surface. For comparison, under illumination, the amount of rhodium(III) adsorbed/reduced is about 55%. While the exact factors are not known, we suggest that this can arise from a combination of different effects such as (a) surface properties of TiO_2 under irradiation, (b) local pH changes under light illumination, and (c) possible photochemical properties of

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(6) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980. (b) A reviewer has suggested that formation of rhodium oxide is unlikely to occur since it requires temperatures above 500 °C. While this may be the expectation for *anhydrous* rhodium oxide, a recent work by Hermann (Hermann, J. M. *J. Catal.* **1984**, *89*, 404) demonstrates that the *anhydrous* compound can also form at ambient temperatures under certain conditions. It is important to note that in this work we are dealing with *hydrated* rhodium oxide which *can form* at ambient temperatures (see ref 5 and 6a).

Table IV. Adsorption of Palladium(II) (ppm) on TiO_2 (100 mg) on Stirring (20 h) a 50-mL Solution in the Dark at Different pHs

Pd(II) (time 0)	Pd(II) (time 20 h)	Pd(II) (adsorbed)[a]	pH
113	109	4	0
81	71	10	3
81	65	16	5
68	0	68	7
70	0	70	10

[a] And/or precipitated.

the $RhCl_3 \cdot 3H_2O$ solutions. Finally, despite the fact that the photoreduction of rhodium(III) is thermodynamically favorable, the process is much slower than the photoreduction of gold(III), suggesting some type of kinetic barrier in the former.

(b) Photochemical Reduction of Palladium(II) on TiO_2. The photochemical reduction of palladium(II) on TiO_2 at pH 3.16 is depicted in Figure 2. Approximately 68 ppm of a palladium(II) solution (air-equilibrated, 10% v/v methanol) was completely reduced within 45 min of simulated sunlight illumination. Oxygen competes with palladium(II) for the conduction band electrons, but its interference is less marked than observed for the rhodium case. At pH >7, the $PdCl_2$ solution turned turbid and a precipitate soon formed. Similar to the experiments carried out on rhodium(III), the pH of the solutions was always kept below 7. Table III summarizes the results of the photoreduction of palladium(II) at various pHs. At pH 0, no reduction occurs even in the presence of CH_3OH (and O_2), at least in the first 45 min of irradiation. At pH >0, reduction takes place with the most efficient rate observed in the pH range 3–5. No doubt, the surface properties of TiO_2 in this range and the interaction of the surface with $PdCl_2$ are important factors, as noted previously for $AuCl_3$ solutions.[3q] A pH profile of the amount of palladium(II) adsorbed on the semiconductor powder or precipitated, by stirring the aqueous slurry in the dark, is reported in Table IV. The pH of the TiO_2 suspensions was adjusted with HCl or NaOH. Parallel experiments in which palladium(II) solutions were brought to different pHs, but in the absence of TiO_2, showed no precipitate(s) formed at pH <7. We conclude that the quantity of palladium(II) removed from solution, by stirring in the dark in the presence of TiO_2, is the result of adsorption at pH <7 and precipitation at pH >7.

(c) Selective Photochemical Reduction of Noble Metals on TiO_2. In this section, we explore the selectivity of the photochemical reduction process on a TiO_2 dispersion in order to selectively separate and recover such noble metals as gold and platinum, as well as rhodium when present in a mixture as might occur in industrial wastes. The parameters that might play a significant role in the reduction step are pH, the presence of oxygen, the presence of an electron donor (e.g. methanol), and the amount of TiO_2 employed.

The results of a typical experiment in which ~30 ppm of gold(III), ~13 ppm of rhodium(III), and ~45 ppm of platinum(IV) were mixed and the resulting air-equilibrated mixture irradiated in the presence of 2 g/L of TiO_2 at pH 7.39 are depicted in Figure 3. The plots summarize the fraction of metal (f_{metal}) remaining in solution as a function of irradiation time. Platinum(IV) was reduced within 10 min of illumination, while gold(III) was reduced within 30 min; in this time frame, rhodium(III) remained in solution, allowing the facile separation of the latter metal from platinum and gold. A major obstacle encountered with rhodium(III) is its hydrolysis and precipitation as $Rh(OH)_3 \cdot nH_2O$ or as $Rh_2O_3 \cdot nH_2O$ at neutral and alkaline pHs.[5,6] Hydrolysis appears to occur more slowly under illumination. Figure 3 shows that hydrolysis and precipitation begin after ~50 min. The presence of methanol, under the same conditions as above, leads to a rapid reduction of gold(III) and platinum(IV) in less than 5 min; however, rhodium(III) is also photoreduced with only 32% remaining in solution. It is important to point out that the presence of oxygen is crucial in preventing the photoreduction of rhodium within the time and conditions of the experiments of Figure 3.

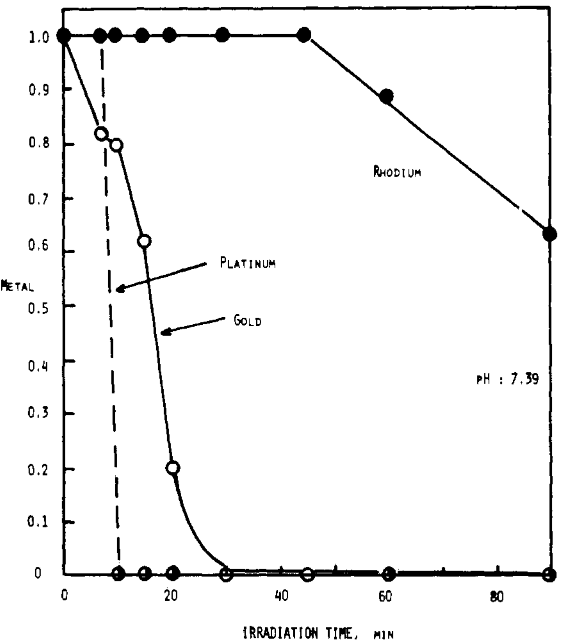

Figure 3. Photochemical separation of Rh(III) (13 ppm) from Au(III) (30 ppm) and Pt(IV) (45 ppm) on TiO_2 (2 g/L). The plots indicate the fraction of the metal remaining in solution as a function of irradiation time. Conditions: AM1 simulated sunlight; pH 7.39; air-equilibriated solutions.

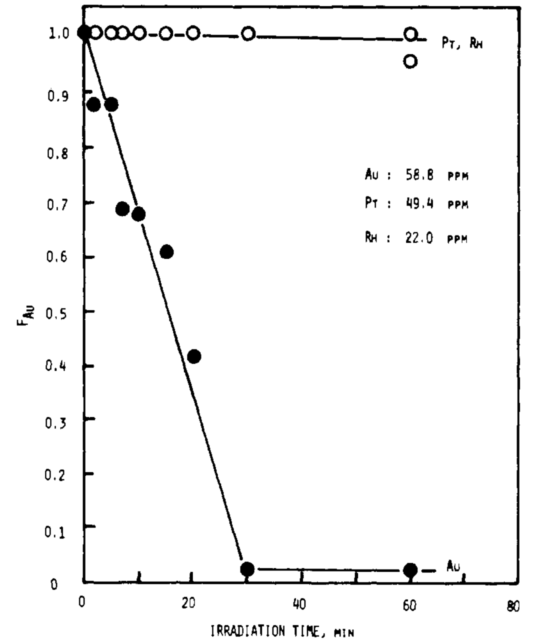

Figure 4. Photochemical reduction and recovery of Au(III) (58.8 ppm) from Pt(IV) (49.4 ppm) and Rh(III) (22 ppm) on TiO_2 (0.2 g/L). The plots show the fraction of metal remaining in solution as a function of illumination time. Conditions: AM1 simulated sunlight; pH 0; air-equilibrated solutions containing 10% v/v methanol.

Selective reduction and recovery can also be obtained from solutions at pH 0. For example, gold(III) is easily photoreduced from air-equilibrated TiO_2 dispersions (0.2 g/L) containing 10% v/v methanol, 58 ppm of gold(III), 49.4 ppm of platinum(IV), and 22 ppm of rhodium(III). The results are summarized in Figure 4, which shows that within 30 min of illumination all of the gold is reduced and deposited on the semiconductor particles; both platinum and rhodium remain in solution. In the absence of methanol, the reduction of gold takes more time. For instance, after 90 min of irradiation, 20% of the initial gold(III) remains in solution. This finding is obtained only when all three metals are in the same mixture because gold(III) is not photoreduced on TiO_2 at pH 0 in the absence of methanol.[3q] The lower con-

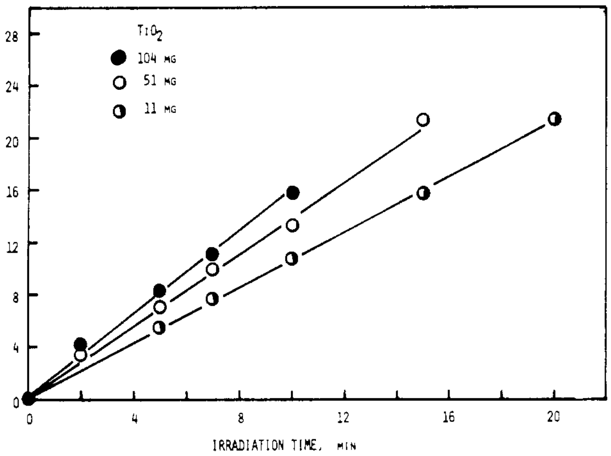

Figure 5. Kinetics of the photoreduction of gold(III) as a function of irradiation time (AM1 simulated sunlight) for three different concentrations of TiO_2 at pH 0. The concentration of Au(0) is described in terms of the initial Au(III) concentration in solution, 2.1×10^{-4} M, with Pt(IV) (27.4 ppm) and Rh(III) (39.7 ppm) present. Conditions: TiO_2 concentration = 0.2, 1, and 2 g/L; 50-mL air-equilibrated solutions containing 10% v/v methanol; pH 0.

centration of TiO_2 in the experiments of Figure 4 (0.2 g/L rather than the usual 2 g/L) was necessitated to minimize the dark adsorption process that would have led to poor selectivity and thus poor separation. It was important therefore to study also the effect of the TiO_2 concentration on the photoreduction. This was investigated for the rate of reduction of gold(III) at three different concentrations of TiO_2 for air-equilibrated solutions containing 10% v/v methanol, 42.1 ppm of gold(III), 27.4 ppm of platinum(IV), and 39.7 ppm of rhodium(III) for which the pH was 0. The data are depicted in Figure 5. The rates of reduction of gold are nearly independent of the quantity of TiO_2 used. In the range 0.2–2 g/L, k increases from 1.8×10^{-7} M s^{-1} to 2.6×10^{-7} M s^{-1} for the highest concentration of TiO_2. The estimated limiting rate is 2.7×10^{-7} M s^{-1}. There was no need to explore the effect at higher concentrations.

In Figure 6, we report the practical separation of platinum(IV) (125 ppm) from rhodium(III) (40 ppm) at pH 2.7 in an air-equilibrated TiO_2 dispersion (2 g/L). Platinum is selectively reduced, leading to facile separation of the two metals. We have also investigated other experimental conditions, but without further improvement. In addition, we considered prior separation of rhodium from the other two noble metals by precipitation of rhodium as $Rh(OH)_3$ or Rh_2O_3 in alkaline solutions. Unfortunately, loss of gold and platinum occurred under these conditions; presumably the metals are trapped in the rhodium precipitate.

Discussion

The mechanisms of the photochemical reduction of platinum(IV)[3d] and of gold(III)[3q] on TiO_2 suspensions have been described previously. To our knowledge, no reports have appeared on the photoreduction of palladium(II) and rhodium(III) over semiconductor dispersions. The photochemistry of the reductive process of Rh(III) and Pd(II) on TiO_2 is complicated by the precipitation of hydroxo or oxo compounds[5] at pH >7.[6] We must point out that the present results apply to solutions of the chloride salts of gold(III), platinum(IV), palladium(II), and rhodium(III). No attempts were made to identify the exact nature of the species in solution. We note however that under the experimental conditions used the species are chloroaquometal complexes of a variety of compositions: $MCl_x(H_2O)_{6-x}$. Our observations and conclusions noted here cannot be extrapolated to other complexes of these metals. For example, photoreduction of gold(III) is different in the presence of cyanide ions.[7]

The Au(III), Pt(IV), Pd(II), and Rh(III) cations present in solutions as the chloride salts are easily photoreduced to the respective metals. The electrochemical redox potential for the reduction process (eq 1), where M is Au, Pt, Pd, and Rh, ranges

$$M(Cl)_x^{(n-x)+} + ne^- \rightarrow M + xCl^- \quad (1)$$

from +1 V (NHE) for gold(III) to +0.4 V (NHE) for rhodium(III).[8] The flat-band potential of TiO_2, V_{fb},[9] which describes the energy of an electron at the TiO_2–electrolyte interface, under equilibrium conditions, is described by

$$V_{fb} = -0.2 - 0.059(pH) \quad (2)$$

The overall photoreduction reaction of a metal ion on TiO_2 is given in eq 3. Although oxygen is the oxidation product, the stoichiometric quantity of oxygen is not always detected because of the photochemical adsorption of O_2 on the surface of the TiO_2 particles.[10]

$$M^{n+} + (n/2)H_2O \xrightarrow[h\nu]{TiO_2} M^0 + nH^+ + (n/4)O_2 \quad (3)$$

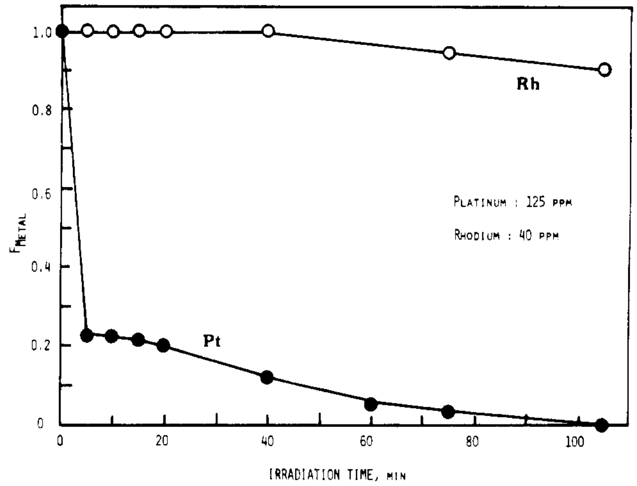

Figure 6. Photochemical separation of Pt(IV) (125 ppm) from Rh(III) (40 ppm) on TiO_2 (2 g/L). The plots show the fraction of the metals remaining in solution as a function of illumination time. Conditions: AM1 simulated sunlight; pH 2.7; air-equilibrated solutions.

Oxygen is detrimental to the photoreduction of rhodium(III) and interferes in the photoreduction of platinum(IV)[3d] and palladium(II), particularly in acidic media where reduction of O_2 is a thermodynamically more favorable process.[8] This was not the case for the photoreduction of gold(III).[3q] The reason for this contrast finds an explanation not only from the driving force[8] of the reduction process, but also from the interaction(s) between the metal and the surface of TiO_2.[11] A general description of this interaction has been given earlier for Au/TiO_2,[3q] and may be extended to Pd(II), Rh(III), and Pt(IV). These metal/TiO_2 interactions, coupled with the thermodynamic and kinetic properties of the systems, have provided the impetus to explore photochemical routes to selectively separate gold, platinum, and rhodium present in dilute solutions as might occur in industrial wastes. As demonstrated in Figures 3, 4, and 6, appropriate conditions of pH, the presence of oxygen, the presence of a valence band hole scavenger, and the amount of the semiconductor dispersion can be explored to obtain preferential reduction of a specific metal over two others in solution to give a complete photochemical separation and therefore recovery of this metal. Moreover, while the three metals we have investigated herein possess the appropriate redox potentials for a favorable photoreduction on TiO_2,[8] they do behave differently in the photore-

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duction process because of the possible interference of oxygen. Their kinetics of photoreduction also appear to be different.

The procedure(s) reported here for the selective separation of gold, platinum, and rhodium is relatively simple and can be extended to the separation of other metals (e.g., silver(I) from palladium(II)). Another parameter that we are investigating[7] is the use of complexing agents, specific for a metal, that might lead to a more efficient or alternative route(s) in the reductive separation of metals on TiO_2.

Summary

We have described a general method for the selective separation of precious metals that is based on commercially available inexpensive materials such as TiO_2,[4] and on AM1 simulated sunlight. We have shown that pH, oxygen, and TiO_2 concentration can vary the rate of deposition of gold, platinum, palladium, and rhodium on TiO_2 and can lead to a differently coated TiO_2 powder. The present results also suggest the possibility of loading semiconductor powders (or colloids) with varying amounts of the noble metals that could find use in photocatalysis,[2c] a direction where much remains to be done to understand the mechanisms and the real potentials of photochemistry to practical and useful applications.

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Registry No. $PdCl_2$, 7647-10-1; $RhCl_3$, 10049-07-7; CH_3OH, 67-56-1; O_2, 7782-44-7; $AuCl_3$, 13453-07-1; H_2PtCl_6, 16941-12-1; Pd, 7440-05-3; Rh, 7440-16-6; Au, 7440-57-5; Pt, 7440-06-4; TiO_2, 13463-67-7.

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Terbium Ion Binding to a Synthetic γ-Carboxyglutamic Acid Containing Heptapeptide Corresponding to Bovine Prothrombin Residues 17–23

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Interactions of terbium(III) with a synthetic γ-carboxyglutamic acid- (GLA-) containing loop corresponding to bovine prothrombin residues 17–23 ($^{17}\text{Gla-}\overline{\text{Cys-Leu-Gla-Gla-Pro-}^{23}\text{Cys}}$) are reported. The results are compared with metal ion binding properties of intact bovine prothrombin fragment 1, bovine prothrombin residues 1–39, and simple Gla- and Gla-Gla-containing peptides. The heptapeptide (Loop) forms a 2:1 metal:peptide complex with dissociation constants of 5.2 and 2.4 μM for the PM and PM_2 complexes. The two Loop-bound terbium(III) ions have each lost approximately 5.6 water molecules from their inner coordination spheres. Addition of excess lanthanum(III) to terbium(III)-containing Loop displaces only a portion of the terbium(III). Analysis of the decay of luminescence of the terbium(III):Loop system in the presence of lanthanum(III) reveals the existence of multiexponential decay, suggesting that the system is no longer in fast exchange on the time scale of the terbium(III) excited-state lifetime. Both the extent of dehydration of Loop-bound terbium(III) ions and the effect of competing ions on exchange between Loop-bound and free aquo ion are more characteristic of the intact protein than of simple Gla-containing peptides. We conclude that the 17–23 structure itself plays a central role in determining the functional metal ion binding properties of the intact prothrombin molecule.

Introduction

Characterization of the interaction of metal ions with the blood-clotting proteins is a matter of considerable importance since it is the metal ion stabilized forms of these proteins that interact with phospholipid-containing cell surfaces and catalyze many of the processes leading to formation of the hemostatic clot.[1] Prothrombin, the zymogen form of the enzyme thrombin, is an excellent model for the study of metal ion interactions with many of these proteins. Near the amino terminus of this protein is a region containing an unusual amino acid, γ-carboxyglutamic acid (Gla). This amino acid is formed by a post-translational vitamin K-dependent carboxylation of glutamyl residues.[2] A considerable number of studies have implicated the Gla residues in the phospholipid binding process, which is essential for function of these proteins in normal blood coagulation.[2]

The Gla-containing region of bovine prothrombin involves at least the first 33 amino terminal residues. The 10 glutamyl residues in this region are all present as Gla. The Gla residues appear three times in this sequence in pairs. The conformational response of the following portion of the bovine sequence (Chart I) has been investigated intensively by experimental and computational methods since isomerization about the ^{21}Gla-^{22}Pro peptide bond has kinetic consequences for protein folding when metal ions are added to the metal ion free protein.[3-6] Since a particular configuration of this loop region is required before appropriate folding in the remainder of the Gla region can occur, leading ultimately to phospholipid binding, it appears that metal ion binding in this region may play an important part in stabilization of the functional structure of prothrombin.

Chart I

$$^{17}\text{Gla-}\overline{^{18}\text{Cys-}^{19}\text{Leu-}^{20}\text{Gla-}^{21}\text{Gla-}^{22}\text{Pro-}^{23}\text{Cys}}$$

Although calcium and magnesium ion binding are of primary importance in in vivo processes involved in blood coagulation,[7]

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