Heterogeneous Photocatalytic Reduction of Ferrate(VI) in UV-Irradiated Titania Suspensions

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The heterogeneous photocatalytic reduction of Fe(VI) in UV-irradiated TiO_2 suspensions was conducted in a basic media. Fe(VI) reduction as a function of TiO_2 suspensions, Fe(VI) concentrations, and pH was studied. The initial rate of Fe(VI) reduction adheres to the simple Langmuir–Hinshelwood kinetics. This and the fractional order with respect to initial Fe(VI) concentrations suggests that the surface reaction is the rate-controlling step. The photocatalytic oxidation of ammonia using TiO_2 in the presence and absence of Fe(VI) was also investigated at pH 9.0. Enhancements in the rates of ammonia oxidation and Fe(VI) reduction were observed. The results indicate the formation of Fe(V) by a TiO_2 conduction band electron. Fe(V) selectively and rapidly oxidizes compounds; therefore, production of Fe(V) by a photocatalytic technique has a role in synthesis and remediation processes.
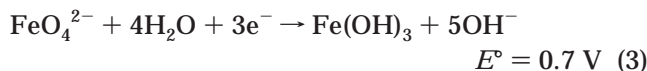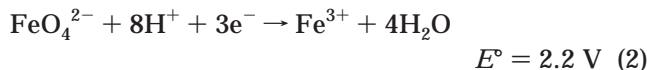
Introduction

The decomposition of inorganic and organic compounds in aqueous suspensions of the highly stable and photo-active semiconductor titanium dioxide (TiO_2) powder has been studied extensively.[1–4] The primary step in this process involves the promotion of an electron from the valence band to the conduction band of the titanium dioxide.[5]

$$TiO_2 \xrightarrow{h\nu} h_{vb}^+ + e_{cb}^- \qquad h\nu > TiO_2 \text{ energy band gap} \tag{1}$$
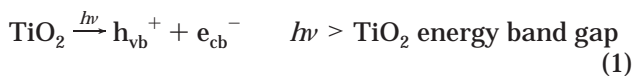
The valence-band holes (h_{vb}^+) and conduction-band electrons (e_{cb}^-) can recombine and dissipate the input energy as heat. The valence band hole is a very powerful oxidizing agent and can oxidize a variety of molecules as well as generating hydroxyl radicals in water, while the conduction band electrons are good reductants. Silver(I), mercury-(II), and chromium(VI) are good examples of oxidants which are reduced by photogenerated electrons of TiO_2 photocatalysis.[6] The photocatalytic conversion of Cr(VI) to Cr(III) has been studied extensively.[7–12]

This paper reports for the first time the photocatalytic reduction of Fe(VI). Fe(VI) has been of great interest because of its role as an environmentally friendly oxidant in remediation and industrial processes.[13–18] Fe(VI) has been hypothesized as a primary candidate in the Martian oxidative pool.[19] A rechargeable super-iron battery using Fe(VI) salts has recently been developed.[20] Fe(VI) species are strong oxidizing agents which can be seen from the reduction potential of reactions 2 and 3 in acidic and alkaline solutions, respectively.[21]

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$$
$$E° = 2.2 \text{ V} \quad (2)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^-$$
$$E° = 0.7 \text{ V} \quad (3)$$

The reduction potential of Fe(VI) in basic solution is more positive than V_{cb} (−0.7 V), and the thermodynamic driving force for the formation of OH^- ions is significantly higher than that of the TiO_2 photocorrosion pathway in basic media.[12] This indicates that the photocatalytic reduction of Fe(VI) in TiO_2 suspensions is feasible. It is likely that the photoreduction of Fe(VI) will take place through three one-electron steps that would result in the sequential formation of Fe(V), Fe(IV), and Fe(III). Fe(V) is 10^3–10^5 times more reactive with compounds than is Fe(VI).[22–24] Fe(V) has also shown selectivity and specificity

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in oxidizing compounds.[23-25] Iron, unlike chromium and manganese, is considered nontoxic; therefore, Fe(V) has a great potential in green synthesis and remediation processes.

Earlier studies used pulse radiolysis techniques to produce Fe(V).[22-27] The use of this apparatus is expensive and limited. In this paper, results are presented that suggest the production of Fe(V) through a photocatalytic technique. The photocatalytic oxidation of ammonia in the presence of Fe(VI) was conducted to indirectly observe the formation of Fe(V) by the photoreduction of Fe(VI) with e_{cb}^- of TiO_2 surfaces.

Experimental Section

All chemicals were reagent or analytical grade and were used as received. The Degusa P-25 TiO_2 (ca. 80% anatase and 20% rutile) was used for the study. Potassium ferrate (K_2FeO_4) of high purity (>98%) was prepared by a wet chemistry method.[28] Doubly distilled ammonium hydroxide (28% ammonia) was used as a source of ammonia.

The reaction vessel was a Pyrex glass 500 mL, three-neck round-bottom flask. The solution was stirred with a magnetic stirrer and a sintered-glass sparging tube attached through one of the necks of the flask. Helium gas was sparged before and during the reactions to create anaerobic conditions in the solution. Oxygen may otherwise have an influence by reacting with a photogenerated electron from TiO_2 to form the superoxide radical[12] ($O_2 + e_{aq}^- \rightarrow O_2^-$, $k = 1.9 \times 10^{10}$ M^{-1} s^{-1}). A glass tube was inserted into one of the necks of the flask to allow excess helium to escape from the reaction solution. A 10 mL syringe was attached to the flask for the removal of samples. The reactor vessel was illuminated with a 15 W ultraviolet lamp (GE, T-15). For each experiment, light intensity was determined using a radiometer (Cole-Parmer 9811) which measured a band of wavelengths (λ) that ranged from 330 to 375 nm with a calibration center of 365 nm. Light intensity in the reaction vessel was calibrated with potassium ferrioxalate actinometry.[29] All experiments were carried out at 22–24 °C.

A 300 mL Fe(VI) solution of desired concentration was illuminated with ultraviolet light for a given period of time. The Fe(VI) solution was prepared by the addition of solid samples of potassium ferrate (K_2FeO_4) to 0.001 M borate/0.005 M phosphate, pH 9.0, where Fe(VI) is most stable. The phosphate serves as a complexing agent for the Fe(III) produced (eq 3), which otherwise precipitates rapidly as a hydroxide that interferes with the optical monitoring of the reaction and accelerates the spontaneous decomposition of Fe(VI). The desired pH was achieved with either phosphoric acid or sodium hydroxide. Different amounts of TiO_2 were suspended in the solution. The experiments were conducted in the pH range 8.5–10.0. The rate of spontaneous decomposition of Fe(VI) in water[30,31] at pH ≥ 8.5 does not contribute significantly to the photocatalytic reduction of Fe(VI) in alkaline medium.

Samples were periodically withdrawn from the reaction vessel and were filtered through a Millipore (0.22 μm) membrane. Fe-(VI) concentration in the samples was determined spectrophotometrically (HP 8452 diode array spectrophotometer). A molar extinction coefficient $\epsilon_{510} = 1150$ M^{-1} cm^{-1} was used for calculating the concentration of Fe(VI) at pH 9.0.[27]

To determine the extent of the photocatalytic reduction of Fe-(VI) due to TiO_2, three different experimental setups were used at each pH: (1) the solution was in contact with the catalyst but kept in the dark; (2) the solution was exposed to UV light in the
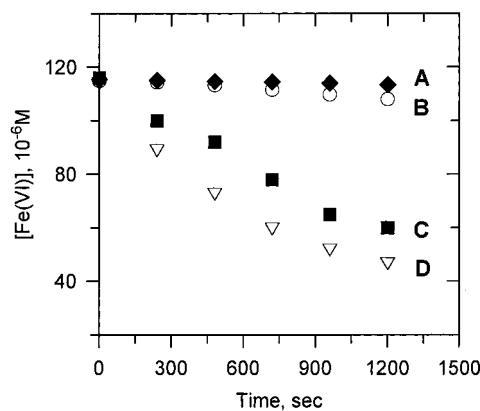

Figure 1. Photocatalytic reduction of Fe(VI) at pH 9.0: A = dark; B = UV only; C = UV + TiO_2 (0.033 g/L); D = UV + TiO_2 (0.066 g/L). Intensity = 328 einstein s^{-1}.

absence of the catalyst; (3) the solution was exposed to UV light in the presence of the catalyst.

A similar experimental setup as described above was used for a study of the photocatalytical oxidation of ammonia in the presence of Fe(VI). The substrate ammonia was chosen because its photocatalytic oxidation has been examined extensively.[32,33] Ammonia photocatalytic oxidation is sluggish, taking hours to complete. The experiment was designed to see whether the reaction can be accelerated with the addition of Fe(VI) in the reaction solution. For each experiment, the reaction solution contained 560 μM Fe(VI) and 940 μM ammonia in 0.001 M borate/0.005 M phosphate. The reaction solution was first purged with helium gas before adding 564 μL of 0.5 M ammonium hydroxide into the reaction solution. The oxidation of ammonia by Fe(VI) was previously studied in our laboratory,[34] and the rate was found to be ≤0.10 M^{-1} s^{-1} in at pH ≥ 8.0. The rate of oxidation of ammonia by Fe(VI) at the specified ratios does not contribute significantly to the photocatalytic TiO_2 oxidation of ammonia. Samples were periodically withdrawn from the reaction vessel, and the concentrations of Fe(VI) and ammonia in the filtered samples (0.22 μm) were determined. The concentration of ammonia was determined by the phenate method.[35]

Results and Discussion

Initially, experiments on photocatalytic reduction of Fe-(VI) were conducted at two different TiO_2 suspension doses as a function of Fe(VI) concentration at pH 9.0. As shown in Figure 1, the photoreduction of Fe(VI) in the TiO_2 suspensions occurred at a faster rate than in the absence of TiO_2. Additionally, photoreduction was greater at higher TiO_2 suspension doses. The photoreduction of Fe(VI) to Fe(OH)$_3$ at TiO_2 surfaces can be expressed by the following equation.

$$FeO_4^{2-} + 4H_2O + 3e_{cb}^- \rightarrow Fe(OH)_3 + 5OH^-$$
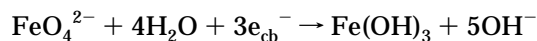
It is unlikely that the photoreduction of Fe(VI) proceeds through a multielectron process. Therefore, it is assumed that the photoreduction of Fe(VI) occurs in successive one-electron steps with the formation of Fe(V) in the first stage (eq 4). Fe(V) has been detected in alkaline media so the assumption is made that Fe(V) was rapidly formed under present experimental conditions. (The observed rate constant for the homogeneous reaction of the hydrated

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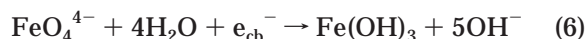(31) Lee, D. G.; Gai, H. *Can. J. Chem.* **1993**, *71*, 1394.

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electron with Fe(VI) is $k = (2.2 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}.[27] Successive one-electron reduction steps will form Fe(IV) and Fe(III) (eqs 5 and 6). The reduction of Fe(VI) to Fe(V) (eq 4) is postulated to be the rate-determining step because of the high instability of Fe(V) and Fe(IV) species, which are reduced at much faster rates than Fe(VI).[21,36]

$$FeO_4^{2-} + e_{cb}^- \rightarrow FeO_4^{3-} \tag{4}$$

$$FeO_4^{3-} + e_{cb}^- \rightarrow FeO_4^{4-} \tag{5}$$

$$FeO_4^{4-} + 4H_2O + e_{cb}^- \rightarrow Fe(OH)_3 + 5OH^- \tag{6}$$

Photoreduction of Fe(VI) at TiO$_2$ surfaces at different Fe(VI) concentrations were analyzed using a plot of log-[initial rate] vs log[Fe(VI)]. Initial rates were obtained using the slope of linear least-squares regression lines of the concentrations of Fe(VI) vs the corresponding time intervals. Initial rates were corrected for the photoreduction of Fe(VI) in the absence of TiO$_2$. A fractional order, 0.32 ± 0.04, with respect to Fe(VI) was found. A similar trend was also observed in the Cr(VI) reduction at TiO$_2$, WO$_3$, α-Fe$_2$O$_3$, and SrTiO$_3$ surfaces.[9] Fractional reaction orders are not uncommon in heterogeneous processes.[37]

The initial rate of disappearance of a variety of organic substrates at illuminated TiO$_2$ surfaces has been described in a Langmuirian form (eq 7) by many workers.[7,37−41]

$$1/rate = 1/k + 1/\{kK[substrate]\} \tag{7}$$

In eq 7, k is the reaction rate constant and K is the apparent binding constant. Some workers have also used Langmuirian analysis to describe chromium(VI) reduction at TiO$_2$ surfaces which are driven by photogenerated holes and reduction reactions.[7] Similar analysis of Fe(VI) reduction data gave a reasonable fit between 1/rate vs 1/[Fe(VI)] ($r = 0.97$) (Figure 2). A value for $k = 3.68 \times 10^{-6}$ M s^{-1} was obtained from the intercept of the data. In comparison, k for the photoreduction of Cr(VI), normalized to TiO$_2$ suspension dose, has been found to be 4.12×10^{-8} M s^{-1} in alkaline media.[7] Generally, Fe(VI) has shown higher reactivity than Cr(VI), which is probably related to a lower E° for Cr(VI) [(CrO$_4^{2-}$/Cr(OH)$_3$) $= -0.12$ V)] than Fe(VI) [(FeO$_4^{2-}$/Fe(OH$_3$) $= 0.72$ V)] in basic media.

Next, experiments were conducted in two TiO$_2$ suspension doses at pH 8.5 and 10.0. Reactions rate constants and binding constants were obtained from Langmuirian plots (Figure 2) and are given in Table 1. Generally, the k values are pH-dependent and decrease with an increase in pH. Literature results suggest the existence of four Fe(VI) species, H$_3$FeO$_4^+$, H$_2$FeO$_4$, HFeO$_4^-$, and FeO$_4^{2-}$, over the entire pH range.[21] The dissociation constants for protonated Fe(VI) species are p$K_1 = 1.6 \pm 0.2$, p$K_2 = 3.5$, and p$K_3 = 7.3 \pm 0.1$.[21] The Fe(VI) species in the studied pH range are HFeO$_4^-$ and FeO$_4^{2-}$. An increase in pH has two combined effects on the photoreduction of Fe(VI) at TiO$_2$ surfaces. The reduction rates of Fe(VI) by substrates decreased with an increase in pH and were largely related to the concentration of HFeO$_4^-$.[13,42,43] An increase in
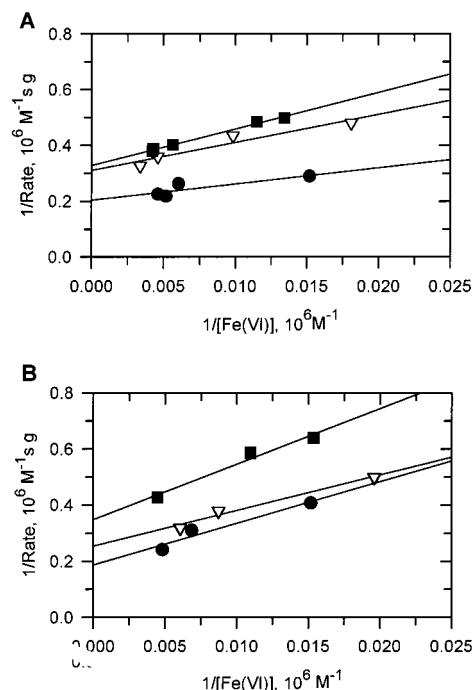
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Figure 2. Langmuir plots at different pH ($\bullet$, pH = 8.5; $\triangledown$, pH = 9.0; $\blacksquare$, pH = 10.0). (A) UV + TiO$_2$ (0.033 g/L); (B) UV + TiO$_2$ (0.066 g/L). Intensity = 328 einstein s^{-1}.

Table 1. Rate Constants (k) and Apparent Binding Constants (K) for Photoreduction of Fe(VI) at TiO$_2$ Surfaces at Different pH

| | TiO$_2$ = 0.033 g/L | | TiO$_2$ = 0.066 g/L | |
| | k ($\times 10^{-6}$ | | k ($\times 10^{-6}$ | |
pH	M s^{-1} g^{-1})	K ($\times 10^4$ M^{-1})	M s^{-1} g^{-1})	K ($\times 10^4$ M^{-1})
8.5	4.6 ± 0.5	4.7 ± 1.4	5.3 ± 0.8	1.3 ± 0.3
9.0	3.3 ± 0.1	3.1 ± 0.3	3.9 ± 0.3	2.0 ± 0.4
10.0	3.1 ± 0.1	2.5 ± 0.1	2.9 ± 0.2	1.7 ± 0.3

electrostatic repulsion between the negatively charged TiO$_2$ surface and the two Fe(VI) species may result from an increase in the more negative FeO$_4^{2-}$ species relative to HFeO$_4^-$ at higher pH values. A combined effect of these processes will result in slower photoreduction of Fe(VI) at TiO$_2$ surfaces with an increase in pH. There is also a possibility of a decrease in the available active sites of TiO$_2$ due to possible adsorption of Fe(OH)$_3$, a product of Fe(VI) photoreduction. However, the complexing phosphate buffer in the present study will help to minimize catalyst poisoning.[44]

Figure 3a shows the oxidation of ammonia in the presence and absence of Fe(VI). The oxidation of ammonia was found to be approximately 3 times faster in the presence of Fe(VI) than with no Fe(VI) in the solution mixture. Literature results do not suggest any significant amount of ammonia adsorption on small micromolar amounts of Fe(III) hydroxide.[45] The photoreduction rate of Fe(VI) also increased in the presence of ammonia in the solution (Figure 3b). Other authors have reported the enhancement effect of ammonium ion on the photocatalytic reduction of Cr(VI).[12]

The enhancement in ammonia oxidation and Fe(VI) reduction can be explained by the suggested reactions in Scheme 1. The following assumptions were made in

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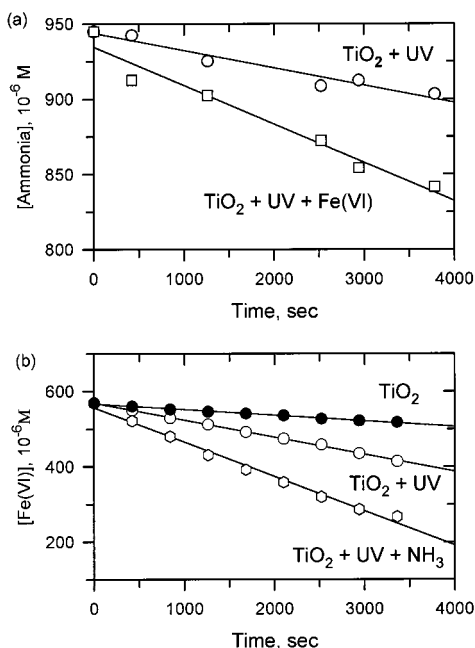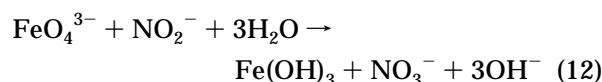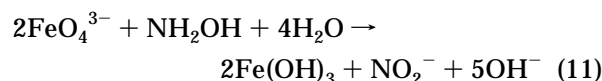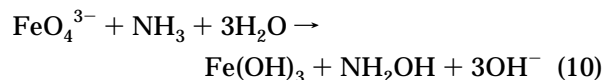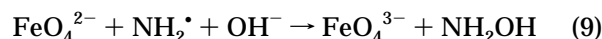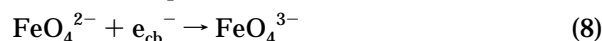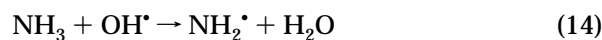(45) Wang, A. Ph.D. Thesis, The University of Toledo, 1991.

Figure 3. Photocatalytic oxidation of ammonia and reduction of Fe(VI) at pH 9.0. $TiO_2 = 0.066$ g/L; intensity = 328 einstein s^{-1}.

Scheme 1

reduction of Fe species

$$FeO_4^{2-} + e_{cb}^- \rightarrow FeO_4^{3-} \qquad (8)$$

$$FeO_4^{2-} + NH_2^\bullet + OH^- \rightarrow FeO_4^{3-} + NH_2OH \quad (9)$$

$$FeO_4^{3-} + NH_3 + 3H_2O \rightarrow$$
$$Fe(OH)_3 + NH_2OH + 3OH^- \quad (10)$$

$$2FeO_4^{3-} + NH_2OH + 4H_2O \rightarrow$$
$$2Fe(OH)_3 + NO_2^- + 5OH^- \quad (11)$$

$$FeO_4^{3-} + NO_2^- + 3H_2O \rightarrow$$
$$Fe(OH)_3 + NO_3^- + 3OH^- \quad (12)$$

oxidation of nitrogen species

$$OH^-_{ad} + h_{vb}^+ \rightarrow OH^\bullet \qquad (13)$$

$$NH_3 + OH^\bullet \rightarrow NH_2^\bullet + H_2O \qquad (14)$$

Scheme 1: (1) equilibrium exists between species of ammonia and Fe(VI) in the bulk solution and at TiO_2

surfaces, and (2) rates of reduction or oxidation of species are not limited by their transport from the bulk solution to TiO_2 surfaces.

In this scheme, the OH$^\bullet$ radical preferentially reacts with ammonia (eq 14) rather than forming hydrogen peroxide by dimerization. This reaction will inhibit the recombination of electrons and holes and thus increase the photocatalytic reduction of Fe(VI). The addition of organic substrates has also been reported to accelerate the photocatalytic reduction of metal ions.[6,46,47] Scheme 1 involves Fe(V), a highly reactive species which is produced by (a) reduction of Fe(VI) by electrons at the conduction band (reaction 8) and (b) amino radical reduction of Fe-(VI) (reaction 9). In homogeneous solution, the rates of Fe(VI) reduction by amino acid radicals[24] are of the order of 10^9 M^{-1} s^{-1}, and it is assumed that the rate constant for reaction 9 will be fast. The amino radical in the proposed Scheme 1 results from the reaction of ammonia with hydroxyl radical, $k = 1 \times 10^8$ M^{-1} s^{-1}; pH 11.4 (reaction 14).[48] Since Fe(V) reacts 3−5 orders of magnitude faster than Fe(VI),[21−25] Fe(V) will react with ammonia to give hydroxylamine (reaction 10). The further reactions of Fe-(V) with hydroxylamine and nitrite will result in nitrate (reactions 11 and 12). Other studies have shown the formation of nitrate as a product in the photocatalytic oxidation of ammonia with TiO_2.[12,32,33] This supports the formation of nitrate as a product in Scheme 1 of our study. Recent work also suggests the formation of nitrate as a product in a similar study using Cr(VI).[12]

Concluding Remarks

Results are presented on a photocatalytic method of producing the highly reactive Fe(V) species, a powerful oxidant, which has the ability to oxidize less reactive substrates such as ammonia. A combination of the oxidant Fe(VI) and the photocatalyst TiO_2 therefore has potential in environmentally friendly syntheses and remediation processes.

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