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Letters

Experimental Evidence in Favor of an Initial One-Electron-Transfer Process in the Heterogeneous Photocatalytic Reduction of Chromium(VI) over TiO_2

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Direct evidence of the involvement of Cr(V) intermediacy in Cr(VI) heterogeneous photocatalytic reduction over TiO_2 was obtained by EPR spectroscopy, in the presence and absence of ethylenediaminetetraacetic acid (EDTA). The rate of formation of Cr(V) becomes rapidly inhibited in the absence of a hole scavenger. Addition of EDTA is found to efficiently suppress the electron-shuttle mechanism by which Cr(VI) reduction is inhibited. Analysis of the data indicates that Cr(V) is formed by a one-electron-transfer process and does not involve Cr(IV) disproportion. It is suggested that Cr(III) formation occurs similarly from Cr(IV) through a charge-transfer mechanism.

Introduction

Heterogeneous photocatalytic reduction of chromium (VI) [Cr(VI) is mutagenic and carcinogenic; inhalation and skin contact of chromium solutions should be avoided] using semiconductors has been extensively investigated, covering aspects such as the activity of different photocatalysts, the influence of the presence of organic donors, the effect of pH and other variables, and the related technology for practical remediation, as cited in the literature.[1−8] However, the features of the complete mechanism have not yet been elucidated. Generally, articles only express the overall process, implicitly assuming a global three-electron-transfer reaction. This possibility is rather unlikely, considering the frequency of photon absorption.[9,10] In recent papers, we have proposed that the actual process occurs via sequential one-electron-transfer steps:[6,11]

$$\mathrm{Cr(VI)} \xrightarrow{e^-} \mathrm{Cr(V)} \xrightarrow{e^-} \mathrm{Cr(IV)} \xrightarrow{e^-} \mathrm{Cr(III)} \qquad (1)$$

Chromium(V) and chromium(IV) species are remarkably unstable and, so far, no direct experimental evidence

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of their involvement in photocatalytic systems is available. Experiments performed by us using a real-time UV−vis spectrophotometric technique under continuous illumination of Cr(VI)/TiO_2 suspensions suggest the formation of Cr(V)/Cr(IV) intermediates.[12]

Electron paramagnetic resonance (EPR) spectroscopy is deemed as a powerful tool for studying Cr(V) transients generated in the reduction of Cr(VI) with organic and inorganic substances. Besides, chromium(V) complexes[13−16] have been receiving special attention in these last years owing to their role in Cr(VI)-induced DNA damage.[16] In this paper, we report the use of EPR spectroscopy to demonstrate Cr(V) intermediacy in the photocatalytic reduction of Cr(VI) and Cr(VI)/EDTA over TiO_2.

Results and Discussion

EPR spectra were obtained at 298 K using a Bruker ER 200 X-band spectrometer (Bruker Analytische Messtechnick GMBH, Germany). 2,2,6,6-Tetramethylpiperidine-1-oxyl (Tempo, $g = 2.0051$) was used as a standard for the determination of g factors, as recommended elsewhere.[17,18] General instrumental conditions were as follows: central field, 3500 G; sweep width, 50 G; scans 1−20; microwave power, 43 mW; modulation frequency, 100 kHz; time constant, 1−50 ms; sweep time, 1−5 s; modulation amplitude, 1.25 Gpp; receiver gain, 8×10^5.

Appropriate volumes of stock solutions of 0.04 M $K_2Cr_2O_7$ and 0.4 M ethylenediaminetetraacetic acid (EDTA) were added to previously sonicated 0.1 g/L aqueous suspensions of TiO_2 Degussa P-25, and the pH was adjusted with diluted $HClO_4$. The samples were irradiated in a quartz cylindrical cell, inside the EPR cavity, with a 400 W medium-pressure metal halide lamp (Philips HPA 400), emitting predominantly between 300 and 450 nm. A 10 cm water cell was used to filter infrared radiation. Control experiments showed that no EPR signal could be detected in the absence of TiO_2, with and without UV irradiation, in the selected conditions of the photocatalytic experiments: $0 \le K_2Cr_2O_7/\mathrm{mM} \le 1.0$, $0 \le \mathrm{EDTA/mM} \le 10.0$, and pH 2.0, on the time scale of our experiments.

The irradiation of a TiO_2 suspension containing 1 mM $K_2Cr_2O_7$ at pH 2.0 gives rise to the transient EPR signal shown in Figure 1. Solid circles indicate the average of five scans (scan time: 1 s^{-1}) between 0 and 5 s after the beginning of irradiation. A rapid decay of the signal occurs under continuous irradiation (open squares), even at negligible Cr(VI) conversions, i.e., at a presumably constant Cr(V) generation rate. However, to keep the photoreduction process going, it is necessary to avoid accumulation of holes or HO radicals on the particles. The one-electron-transfer process through which Cr(V) is generated from Cr(VI) has as conjugate reaction the water oxidation process by holes:

$$H_2O + h^+ \rightarrow HO^\bullet + H^+ \tag{2}$$

As soon as chromium(V) is formed, its oxidation by $HO^\bullet$ or by holes (competing with (2)), is a rather likely process:

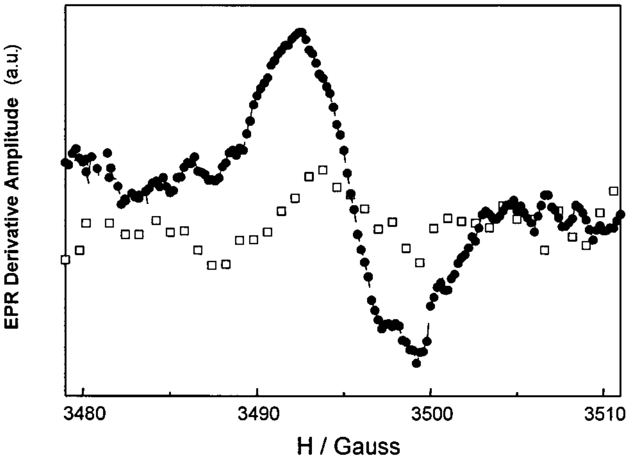

Figure 1. EPR spectra of the intermediates formed under continuous irradiation of a TiO_2 suspension containing 1 mM $K_2Cr_2O_7$ at pH 2.0. The data are the average of five scans (scan time, 1 s^{-1}) between 0 and 5 s (solid circles) and between 40 and 45 s (open squares).

$$Cr(V) + h^+ (HO^\bullet) \rightarrow Cr(VI)\ (+\ HO^-) \tag{3}$$

Thus, the temporal evolution of the EPR signal may be explained by the electron-shuttle mechanism outlined above and is in agreement with stationary experiments previously performed, which indicate a rapid inhibition of chromium(VI) reduction in the absence of added donors.[4,6,11]

The addition of 10 mM EDTA to the TiO_2 suspension containing 1 mM $K_2Cr_2O_7$ at pH 2.0 produces, upon irradiation, the EPR spectra shown in Figure 2. In this case, EDTA will react with holes and/or hydroxyl radicals

$$RCOOH + h^+ (HO^\bullet) \rightarrow RCOO^\bullet + H^+ (H_2O) \tag{4}$$

competing favorably with reaction (3) and suppressing the electron-shuttle mechanism. Now, the signal remains unchanged during the first minutes of irradiation, indicating that, in this case, no decrease of the rate of Cr(VI) reduction occurred, a fact already observed in the stationary photocatalytic experiments in the presence of hole scavengers as EDTA.[4,6,11]

A recent analysis has shown that the measured ^{53}Cr hyperfine values, A_{ISO}, and g_{ISO} values of Cr(V) complexes in solution can be used to elucidate structures associated with paramagnetic signals.[14] However, the assignment of the structures that give rise to the signals in Figures 1 and 2 is complicated by the fact that the features of the spectra depend on the tumbling rates of the species and, in this case, may be constrained by radical adsorption. Thus, we will not attempt to make a definitive assignment. Instead, we will report the experimental g values obtained in the heterogeneous system, relative to that of Tempo, and mention the related information available for the homogeneous system.

For the spectrum in Figure 1, we determined a value of $g = 1.9707$, which is very close to that reported for a freely tumbling $[Cr(O)(H_2O)_5]$ in solution.[14]

On the other hand, the paramagnetic signal obtained in the presence of EDTA shows two rather well-defined peaks (Figure 2). Cr(V)/EDTA complexes are not characterized in the literature. To our knowledge, the only report of an EPR spectrum ($g = 1.969$) of a system containing Cr(VI) and EDTA was obtained after reaction

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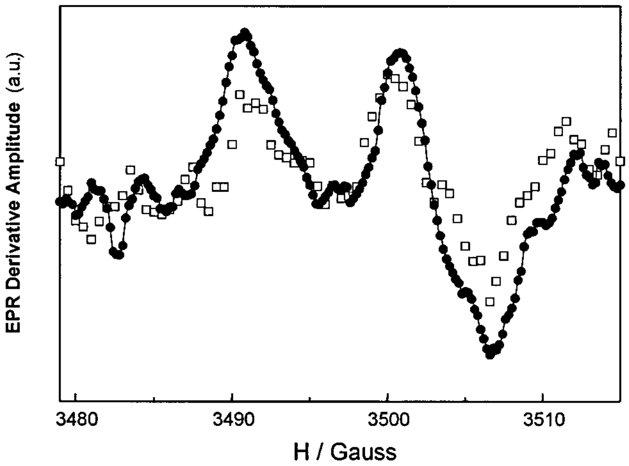

Figure 2. EPR spectra of the intermediates formed under continuous irradiation of a TiO_2 suspension containing 10 mM EDTA and 1 mM $K_2Cr_2O_7$ at pH 2.0. The data are the average of five scans (scan time, 1 s^{-1}) between 0 and 5 s (solid circles) and between 115 and 120 s (open squares).

with Co(II) and tentatively assigned to Cr(V)/EDTA.[19] From data in Figure 2, we estimated $g = 1.9664$ for the peak at higher fields, in close agreement with the above value. Moreover, an attempt to synthesize the paramagnetic complex in solution was made in a different way. In a separate experiment, 0.08 M Cr(VI) and 0.1 M EDTA were allowed to react at pH 2, in the dark, and in the absence of TiO_2. In contrast to experiments performed at low concentrations of the reagents, used in the photocatalytic runs, a paramagnetic signal appeared clearly, presenting $g = 1.9659$. Figure 3 depicts the spectra of heterogeneous and homogeneous systems (upper and lower parts, respectively) obtained in this work. It can be speculated that the peak at lower fields in the heterogeneous system arises from the contribution of two different structures, that of Cr(V)/EDTA and the other of some peroxo- or aquo-Cr(V) complex. However, additional work is in progress in order to perform a definitive assignment.

Further analysis of our data provides some additional insights on the mechanism of chromium(VI) reduction. At longer irradiation times, the broad and intense EPR signal (spectral width ~ 770 G) corresponding to Cr(III) (not shown) was clearly detected. Though Cr(IV) cannot be detected by EPR spectroscopy, the possibility of its disproportion (reaction (5)) is ruled out by the fact that Cr(III) and Cr(V) species could not be detected simultaneously in the course of the photocatalytic experiments.

$$2\mathrm{Cr(IV)} \rightarrow \mathrm{Cr(V)} + \mathrm{Cr(III)} \qquad (5)$$

This indicates that Cr(V) is unequivocally generated through a one-electron-transfer process and not through reaction (6), followed by (5). Consistently, Cr(III) generation cannot be ascribed to process (5).

$$\mathrm{Cr(VI)} \xrightarrow{2e^-} \mathrm{Cr(IV)} \qquad (6)$$

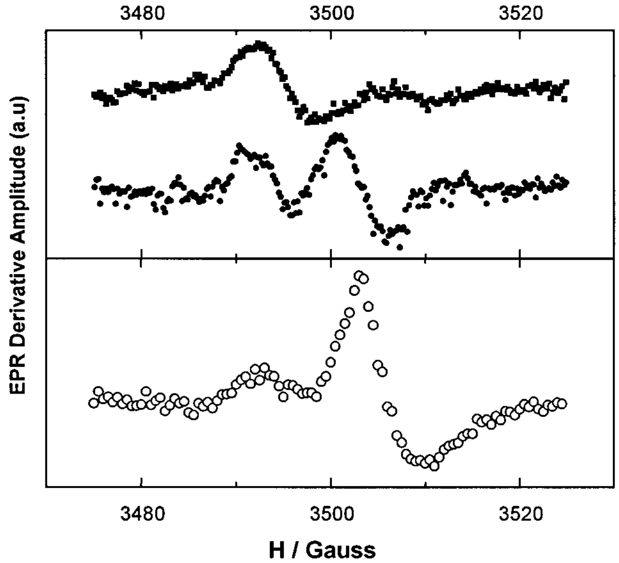

Figure 3. EPR spectra of the Cr(V) intermediates. The upper graph corresponds to the spectra obtained under UV irradiation of a 0.1 g/L TiO_2 suspension containing 1 mM $K_2Cr_2O_7$ at pH 2.0 for (a) [EDTA] = 0 and (b) [EDTA] = 10 mM. The lower graph shows the signal formed upon mixing equal volumes of 0.08 M Cr(VI) and 0.1 M EDTA solutions in the dark at pH 2. Estimated g factors are discussed in the text.

While step (6) cannot be discarded on the basis of experimental evidence, similarly to process (7), both

$$\mathrm{Cr(V)} \xrightarrow{2e^-} \mathrm{Cr(III)} \qquad (7)$$

reactions involve two-electron-transfer reactions, which are very improbable processes in photocatalytic systems over small particles, as was already stated.

In summary, this work shed light on the mechanism of Cr(VI) photocatalytic reduction, providing clear evidence of an initial one-electron transfer to Cr(V) and no disproportion of Cr(IV). Further spectroscopic work to account for the remaining unresolved issues is currently underway.

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