ARTICLES

Magnetic Field Effect on the Photocatalytic Reaction with Ultrafine TiO$_2$ Particles

Masanobu Wakasa,*,† Sachiko Suda,† Hisaharu Hayashi,§ Nobuharu Ishii,‡ and Mitsutoshi Okano‡

Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Sakura-ku, Saitama-shi, Saitama 338-8570, Japan, Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima, Tokyo 171-8588, Japan, and Department of Nanochemistry, Faculty of Engineering, Tokyo Polytechnic University, Iiyama, Atsugi, Kanagawa 243-0297, Japan

Magnetically induced acceleration of a photocatalytic reaction was observed for the first time. Upon irradiation of ultrafine TiO$_2$ particles in *tert*-butyl alcohol at room temperature, the decomposition reaction of *tert*-butyl alcohol generated acetone and methane as the main products. The yield of acetone was found to increase with increasing magnetic field from 0 to 1.5 T. An increase of about 10% in the yield was observed at 1.5 T. The observed magnetic field effects can be explained by the magnetically induced blocking of the recombination of electrons and holes in the semiconductor.

Introduction

Since the discovery of photoelectrochemical decomposition of water into hydrogen and oxygen by Honda and Fujishima in 1972,[1,2] the photochemistry and photophysics of semiconductors, especially those of TiO$_2$, have gained much attention. Studies of both fundamental aspects and practical applications have been carried out extensively.[3] It is well-known that the strong oxidation and reduction power of such semiconductors can be used to effect changes in organic molecules as well as to convert light energy into different types of energy. In all such studies, the efficiency has been of utmost significance. To improve the efficiency of light energy and material conversion, (1) the separation of the photogenerated holes and electrons (a physical process) and (2) the back reaction of the products (a chemical process) are both important.[4] In electron-transfer reactions, it is known that magnetic fields can affect the recombination process of cation and anion radicals, and such magnetic field effects have been studied widely.[5] Therefore, by considering the similarities between photocatalytic reactions and electron-transfer reactions, the authors wished to utilize magnetic fields to raise the efficiency of photocatalytic reactions on semiconductor particles. There are, however, few reports for such magnetic field effects on photocatalytic reactions. In 1983, Kiwi reported magnetic field effects on a photosensitized electron-transfer reaction in the presence of TiO$_2$ and CdS loaded particles.[6] In this report, a suspension of TiO$_2$ and CdS particles was used and a decrease in H$_2$ evolution was found to occur in the presence of magnetic fields below 0.4 T.

To date, many photocatalytic reactions have been carried out with suspensions of semiconductors particles. Under such inhomogeneous, opaque conditions, however, the efficiency of the energy conversion is much smaller than that under homogeneous, transparent conditions. In our preliminary results on the photocatalytic decomposition of *tert*-butyl alcohol with platinized TiO$_2$ particles (100−300 μm), a magnetic field effect on the product yield was observed, but the decomposition reaction was very slow and the experimental errors in the product yields were as large as 5−10%.[7]

To enhance the reaction efficiency and to avoid poor experimental reproducibility, we synthesized ultrafine colloidal TiO$_2$ particles substituted with a hydrophobic coupling agent and studied the magnetic field effect on the photocatalytic decomposition reaction of *tert*-butyl alcohol with these particles. In this paper, we report that an increase in the yield of one of the main products, acetone, was observed with the application of a 1.5 T magnetic field. Therefore, it seems possible that the efficiency of the energy conversion in the process might be enhanced by ordinary magnetic fields.

Experimental Section

The ultrafine colloidal TiO$_2$ particles were synthesized by the coupling of titanium tetraisopropoxide (TTIP) and isopropyl tris(dioctyl pyrophosphate) titanate (coupling agent) in aqueous ethanol as described in the literature.[8] In this work, the molar ratio of the coupling agent and TTIP was 0.1 and the mixed solution was refluxed for 5 h. The TiO$_2$ particles obtained were dispersed and transparent in methanol, ethanol, *tert*-butyl alcohol, and acetone. The particle sizes were measured to be 21−43 and 25 nm (mean diameter of the area distribution) by TEM and DLS (dynamic light scattering), respectively.

Magnetic fields (*B*) of up to 1.5 T were provided by a Tokin SEE-10W electromagnet. The lowest magnetic field, generated by applying a counter-current to cancel the residual field, was less than 0.05 mT. Hereafter, the experiments under the lowest field are denoted as those in the absence of a magnetic field.

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* Address correspondence to this author. E-mail: mwakasa@chem.saitama-u.ac.jp.
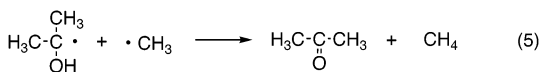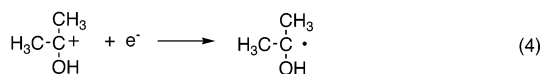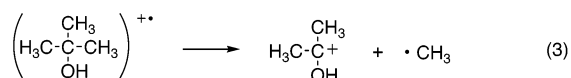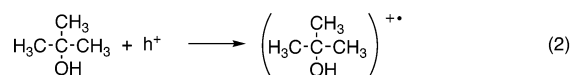† Saitama University.
§ Gakushuin University.
‡ Tokyo Polytechnic University.

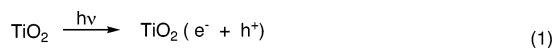Photocatalytic Reaction with Ultrafine TiO₂ Particles

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To measure magnetic field effects on photocatalytic reactions with ultrafine TiO$_2$ particles, we choose the photocatalytic decomposition reaction of neat *tert*-butyl alcohol, as it has a simple and well-studied reaction mechanism.[9] The synthesized ultrafine colloidal TiO$_2$ particles (typically 15 mg) and *tert*-butyl alcohol (2 mL) were placed in a quartz cell (10 mm) with a PTFE-rubber septum. Each of the solutions was irradiated with a 500-W deep UV lamp at room temperature, in the absence and presence of magnetic fields. The lamp intensity was continually measured by a power meter and its fluctuation was within 1%. UV–vis spectra were recorded with a Shimadzu UV-2550 spectrometer.

At 1 h after irradiation, the products were analyzed by GLC and GC-MS. Acetone and methane were generated as the main products. Although hydrogen is believed to be generated, its yield is very low under the present nonaqueous conditions. Quantitative analysis of acetone was carried out by GLC as follows: A Shimadzu GC-14B gas chromatograph coupled with a Shimadzu AOC-20i auto-injector was used with a RESTEK Stabilwax-DB capillary column (15 m, 0.25 mm ID, 0.25 μm df). The chromatograph was recorded with a Shimadzu chromatopac C-R6A integrator. The yield of acetone (Y) was determined with decane as an internal standard.

Results and Discussion

Reaction Scheme. In the present reaction, the electron (e$^-$) and the hole (h$^+$) are generated by irradiation of TiO$_2$ (eq 1). Oxidation of *tert*-butyl alcohol occurs by reaction with the photogenerated hole to generate its cation radical (eq 2). The cation radical decomposes to a 2-propanol cation and a methyl radical (eq 3). There is also the possibility that the cation radical decomposes to a 2-propanol radical and a methyl cation. Since the mass fragment of the 2-propanol cation is much larger than that of the methyl cation, from the GC-MS analysis of *tert*-butyl alcohol we are able to conclude that the decomposition of a cation radical to a 2-propanol radical and a methyl cation is less dominant than reaction 3 in the present reaction. Next, the 2-propanol cation is reduced by an electron to form a 2-propanol radical (eq 4). Finally, a disproportionation reaction occurs between the 2-propanol and methyl radicals to form acetone and methane (eq 5).

$$TiO_2 \xrightarrow{h\nu} TiO_2\,(e^- + h^+) \tag{1}$$

$$\text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\text{-CH}_3 + h^+ \longrightarrow \left(\text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\text{-CH}_3\right)^{+\bullet} \tag{2}$$

$$\left(\text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\text{-CH}_3\right)^{+\bullet} \longrightarrow \text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}^+ + \cdot\text{CH}_3 \tag{3}$$

$$\text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}^+ + e^- \longrightarrow \text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\cdot \tag{4}$$

$$\text{H}_3\text{C-}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\cdot + \cdot\text{CH}_3 \longrightarrow \text{H}_3\text{C-}\underset{\text{O}}{\overset{\text{CH}_3}{\text{C}}}\text{-CH}_3 + \text{CH}_4 \tag{5}$$

Magnetic Field Effect. Quantitative analysis of acetone was carried out by GLC. The photocatalytic decomposition reaction of *tert*-butyl alcohol with the ultrafine colloidal TiO$_2$ particles was performed in the absence and presence of an external magnetic field of 1.5 T. The yields of acetone (Y) observed are

TABLE 1: Yields of Acetone ($Y(B)$) and Relative Magnetic Field Effects ($R(B)$) Observed at Room Temperature for the Photocatalytic Decomposition Reaction of *tert*-Butyl Alcohol with Ultrafine Colloidal TiO$_2$ Particles in the Absence and Presence of an External Magnetic Field of 1.5 T

run	$Y(B)$/mmol[a]		$R(1.5\ \text{T}) =$
	$B = 0\ \text{T}^b$	$B = 1.5\ \text{T}$	$Y(1.5\ T)/Y(0\ T)$
1	0.0416	0.0470	1.13
2	0.0386	0.0443	1.15
3	0.0396	0.0446	1.13
4	0.0452	0.0492	1.09
5	0.0414	0.0474	1.14
av			1.13 ± 0.02^c

[a] The yield of acetone was obtained from 5 or 10 separate chromatograms for each reaction solution. Experimental errors were within ±0.001 mmol. [b] The lowest magnetic field was generated by application of a counter-current to cancel the residual field, and was less than 0.05 mT. The experiments in such a field are denoted as those in the absence of a magnetic field. [c] Standard deviation.
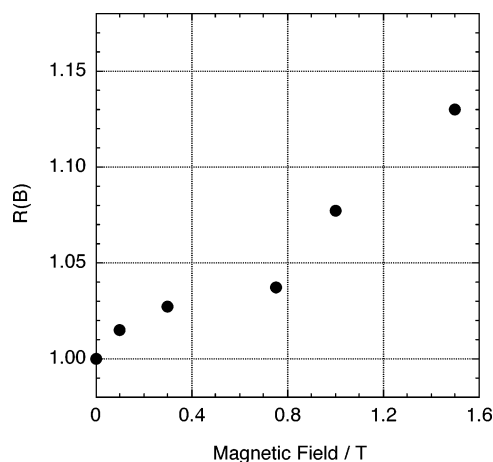

Figure 1. Magnetic field dependence of the relative magnetic field effect ($R(B) = Y(B)/Y(0\ \text{T})$) observed at room temperature for the photocatalytic decomposition reaction of *tert*-butyl alcohol with the ultrafine colloidal TiO$_2$ particles in the absence and presence of external magnetic fields of varying magnitude.

listed in Table 1. The relative magnetic field effect observed at 1.5 T, $R(1.5\ \text{T})$, is represented as follows:

$$R(1.5\ \text{T}) = Y(1.5\ \text{T})/Y(0\ \text{T}) \tag{6}$$

The $R(1.5\ \text{T})$ values obtained are also listed in Table 1. This table shows that the yield of acetone increases by about 10% with increasing magnetic field from 0 to 1.5 T. To the best of our knowledge, this is the first report of the magnetically induced acceleration of a photocatalytic reaction. Although Kiwi reported magnetic field effects on photosensitized electron-transfer reactions in the presence of TiO$_2$ and CdS loaded particles, the magnetic field decelerated the evolution of H$_2$. Furthermore, Kiwi found no magnetic field effect on the direct photolysis with TiO$_2$ and CdS. The effects were only observed in the presence of Ru(bpy)$_3{}^{2+}$.[6]

Mechanism of the Magnetic Field Effects. To clarify the mechanism of the magnetic field effect, we measured the magnetic field dependence of the relative magnetic field effect $R(B)$ for fields between 0 and 1.5 T. The observed $R(B)$ values are plotted against B in Figure 1. It is clear that the $R(B)$ value gradually increases with increasing B from 0 to 1.5 T. The observed magnetic field effects may occur during either the reencounter of free radicals[5] or the recombination of electrons and holes.

First, consider magnetic field effects on the recombination of free radicals. The triplet and singlet radical pairs are generally formed in a three-to-one ratio when the free 2-propanol and methyl radicals reencounter (free radical precursor). The singlet radical pair immediately reacts to form the disproportionation products of acetone and methane (cage products). Since the triplet radical pair cannot react directly, the radicals either escape from the triplet pair or undergo spin-state mixing to produce a singlet pair by the hyperfine coupling and the Δg mechanisms (HFCM and ΔgM).[5] In the case of the HFCM, the yield of cage products from a free radical precursor should decrease with increasing magnetic field.[5] Moreover, magnetic field effects caused by the HFCM are usually saturated below 50 mT.[5] As shown in Figure 1, however, the yield of acetone increases with increasing magnetic field and no saturation is observed below 1.5 T. From these results, we conclude that the present magnetic field effects are not due to the HFCM and that the HFCM can be safely excluded from consideration.

In the case of the ΔgM, the yield of cage products from a free radical precursor should increase with increasing magnetic field. Thus, the yield of acetone should increase with increasing magnetic field under the ΔgM. However, in our preliminary results for the photocatalytic decomposition of *tert*-butyl alcohol with platinized TiO$_2$ particles (anatase, particle size 100−300 μm),[7] the yield of acetone was found to decrease with increasing magnetic field from 0 to 1.5 T. Similar reversed magnetic field effects have also been reported for the photocatalytic reaction of platinized TiO$_2$ particles by Tanimoto et al.[10] As the magnetic field effects observed with platinized TiO$_2$ particles[7,10] are in the opposite sense to those observed with the ultrafine colloidal TiO$_2$ particles, we can conclude that the magnetic field effects observed in both cases are not caused by the reactions of free radicals generated by the photocatalytic decomposition reaction of *tert*-butyl alcohol, as this should be the same for both particle types.

Thus another suitable candidate for the explanation of the observed magnetic field effects is the magnetically induced blocking of the recombination of electrons and holes in the semiconductor. In this case, the observed magnetic field effect can be explained by the ΔgM only if the electron exchange interaction is small or zero. A small exchange interaction has been proposed for the magnetic field effect on the recombination of positive and negative polaron pairs in poly(phenylene vinylenes).[11]

The geminate singlet pairs of electrons and holes generated by irradiation of ultrafine colloidal TiO$_2$ particles recombine with one another, but they can partially react with *tert*-butyl alcohol (eq 2) and 2-propanol cation (eq 4). The singlet pairs of electrons and holes can convert to triplets, and this conversion can be accelerated by a magnetic field through the ΔgM. The triplet pairs of electrons and holes cannot recombine and they escape from the pair, reacting with *tert*-butyl alcohol and 2-propanol cation on the surface of the semiconductor. Thus the observed magnetic field effect can be explained by magnetically induced blocking of electron−hole recombination.

To confirm such a possibility, we also measured the UV−vis spectra of *tert*-butyl alcohol containing ultrafine colloidal TiO$_2$ particles upon irradiation. The UV−vis spectrum observed at 1 h after irradiation in the absence of a magnetic field is shown in Figure 2. The observed spectrum has a broad absorption band at 400−700 nm with a lifetime as long as a few hours in deaerated *tert*-butyl alcohol. Moreover, the broad band is immediately quenched on exposure to air. We can safely assign the observed spectra to trapped electrons in comparison
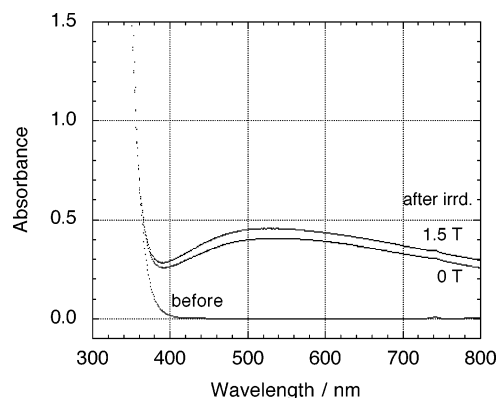

Figure 2. UV−vis spectra of *tert*-butyl alcohol solutions containing ultrafine colloidal TiO$_2$ particles observed at room temperature before irradiation (bottom) and at 1 h after irradiation under 0 (middle) and 1.5 T (top), respectively.

with previous reports on trapped electrons.[12−14] For example, Kamat et al. observed a similar long-lived UV−vis spectrum with a conventional spectrometer upon irradiation of a deaerated suspension of TiO$_2$ colloids in ethanol containing 6% acetic acid.[12] They assigned the observed spectrum to trapped electrons for the following reasons: (1) The absorption band agrees well with previously reported spectral features (wavelength and lifetime) of trapped electrons.[14] (2) The band disappears in the presence of electron scavengers (O$_2$ and C$_{60}$). (3) In a nanosecond laser flash photolysis experiment, both a fast decay (due to recombination of electrons and holes) and a near constant signal (due to stable, trapped electrons) were observed.

Trapped electrons are generated on the colloidal TiO$_2$ surface when electrons and holes react with *tert*-butyl alcohol and 2-propanol cation radicals. If the magnetic field effects observed in this system are indeed due to a change in the rate of electron−hole recombination, then the application of a magnetic field of 1.5 T should also produce an increase in the number of trapped electrons. The spectrum observed at 1 h after irradiation in the presence of a magnetic field of 1.5 T is also shown in Figure 2. We can see from this figure that the intensity of the spectrum increases by about 10% with the application of a 1.5 T field. Equivalent magnetic field effects on the UV−vis spectra were also observed under 0, 0.75, and 1.0 T. These results indicate that the yield of trapped electrons increases with increasing magnetic field and that the magnetic field effect does indeed likely occur during the recombination of electrons and holes. Since the magnetic field effects are believed to be caused during the recombination of geminate singlet electron−hole pairs, the effect should be observed on a picosecond time scale. However, since trapped electrons have a long lifetime, it is possible to observe the magnetic field effects on a much longer time scale by using a typical UV−vis spectrometer.

Conclusion

A magnetic field effect on the photocatalytic reaction of *tert*-butyl alcohol with ultrafine colloidal TiO$_2$ particles was observed. The yield of the main product acetone increases with increasing magnetic field from 0 to 1.5 T, producing about a 10% increase at 1.5 T. The yield of trapped electrons was also found to increase with increasing magnetic field. It is noteworthy that this is the first report of magnetically induced acceleration of a photocatalytic reaction. The acceleration of photocatalytic reaction observed for the present study can be explained as a magnetic field effect on the recombination of electrons and holes through the Δg mechanism.

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References and Notes

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Since the size of the particles in the present reaction is as small as 21−43 nm, the quantum size effect (Li, X.; Quan, X.; Kautal, C. *Scr. Mater.* **2004**, *50*, 499) might be expected.

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