Photocatalysis

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Visible-Light-Induced Aerobic Oxidation of Alcohols in a Coupled Photocatalytic System of Dye-Sensitized TiO_2 and TEMPO**

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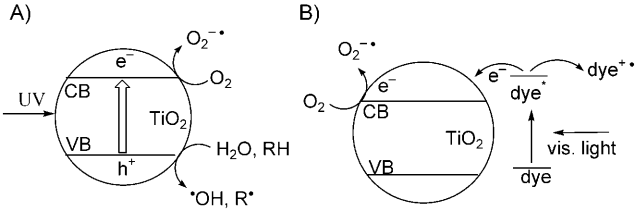
Selective catalytic oxidation of alcohols is a fundamental transformation for the synthesis of fine chemicals.[1] Catalysts based on transition metals, such as palladium, platinium, and copper, have been used for efficient aerobic oxidation of alcohols.[2] Selective transformation of alcohols by dioxygen can also be achieved in the presence of both transition-metal ions and nitroxyl radicals (such as 2,2,6,6-tetramethylpiperidinyloxyl, TEMPO).[3] However, the use of large amounts of transition-metal complexes could potentially lead to environmental pollution. Therefore, considerable efforts have been made to find a clean catalytic system without transition metals for the aerobic transformation of alcohols. Recently, a novel transition-metal-free TEMPO-based catalysis system was developed, in which Br_2 and $NaNO_2$ were used as cocatalysts, and the effective oxidation of alcohols by molecular oxygen was accomplished at 80 °C.[4a] To facilitate the removal of the TEMPO catalyst after use, a heterogeneous variant in which TEMPO is supported on SBA-15 was prepared; this, together with $NaNO_2$ as cocatalyst, was also used successfully for the selective oxidation.[4b]

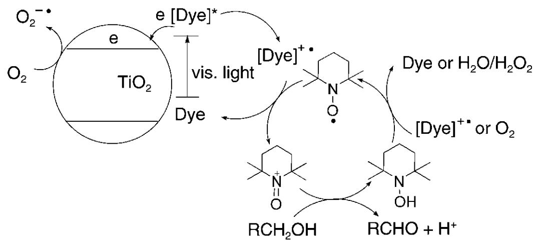
The TiO_2 photocatalyst under UV irradiation is a clean catalytic system widely applied for degradation of organic pollutants by dioxygen. However, for organic synthesis, the selectivity of the TiO_2-photocatalyzed oxidation is unsatisfactory.[5] In photooxidation processes, the photo-generated holes in the valence band of TiO_2 have high oxidative potential (2.7 V) and propel the oxidation of the organic compounds (Scheme 1 A). But they may oxidize reactant alcohols and product aldehydes (or ketones) indiscriminatingly, resulting in a poor selectivity for the product aldehydes.[5,6] The selectivity problem actually impedes the application of TiO_2 photocatalysis for the synthesis of fine chemicals. To achieve high product selectivity for alcohol oxidation using TiO_2 photocatalyst, one must avoid the formation of strongly oxidative holes in the valence band of TiO_2. Novel systems are required that can conduct alcohol oxidation but not generate holes under irradiation.



Scheme 1. The mechanisms of A) TiO_2 photocatalysis under UV irradiation and B) the dye/TiO_2-sensitized reaction under visible-light irradiation. CB: conduction band, VB: valence band.

We and others have found that the dyes undergo effective photosensitized degradation in water in the presence of TiO_2 under visible-light irradiation.[7] In the dye-sensitized system, the dye, rather than the TiO_2 catalyst, absorbs visible light and is excited (Scheme 1 B). More importantly, the visible-light irradiation will not create holes in the valence band of TiO_2. This is distinctly different from the situation of TiO_2 photocatalysis under UV irradiation (Scheme 1 A). In the dye/TiO_2-photosensitized reaction, the conduction band of TiO_2 still plays an important role. The appropriate potential relation enables the excited dye molecules to inject electrons into the conduction band of TiO_2 particles, yielding dye radicals (Scheme 1 B).[7] These dye radicals are transient, active species and decompose to small molecules and even further to CO_2 by complicated dioxygen-involved reactions.

The nitroxyl radical TEMPO can act as an electron donor and be oxidized to $TEMPO^+$, which is an effective and selective oxidant for the transformation of primary alcohols into aldehydes by a two-electron-transfer mechanism.[3] The produced TEMPOH can regenerate TEMPO by reaction with the oxidative dye radials or O_2.[3a,c] The combination of dye-sensitized TiO_2 and TEMPO thus offers an interesting hypothesis: if dye-sensitized TiO_2 can drive the electron-transfer cycle of TEMPO ($TEMPO \rightarrow TEMPO^+ \rightarrow TEMPOH \rightarrow TEMPO$), we should be able to develop a clean catalytic system for the selective oxidation of alcohols.



Scheme 2. The proposed visible-light-induced reaction cycles in the dye/TiO_2/TEMPO system.

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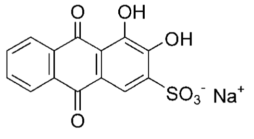
Such a photocatalytic system can exhibit good selectivity (owing to TEMPO), operate under visible-light irradiation at ambient temperature, and use molecular oxygen (because of the dye-sensitized TiO_2). The prerequisite is that the dye radicals arising from the dye-sensitized TiO_2 under visible light are effectively and rapidly quenched by TEMPO through an appropriate intermolecular interaction. Dioxygen can trap the electrons in the conduction band of TiO_2 to form $O_2^{-\bullet}$, H_2O_2, or H_2O. Scheme 2 illustrates the principles of the coupling redox cycles for the photocatalytic and selective oxidation of alcohols under visible-light irradiation.



Alizarin Red (AR)

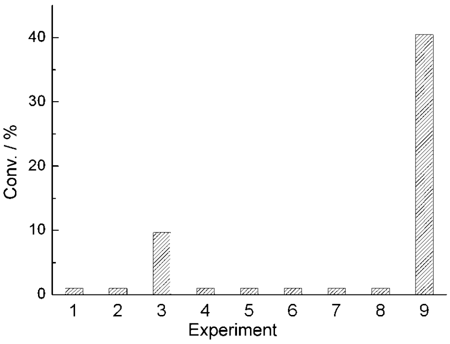
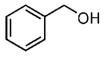
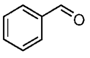
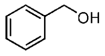
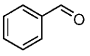
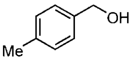
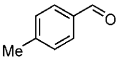
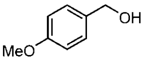
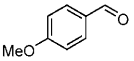
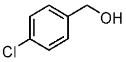
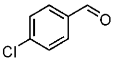
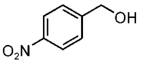
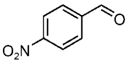
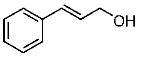
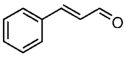
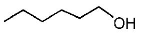
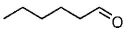
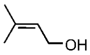
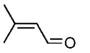
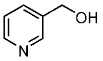
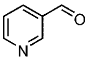
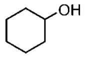
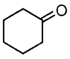


Figure 1. Control experiments for the transformation of benzyl alcohol (0.1 mmol in 1.5 mL BTF) under different conditions; the reaction time was 6 h. Experiments 1: AR/TiO_2/TEMPO $+O_2$, in the dark; 2: AR + TEMPO + O_2, visible light; 3: AR/TiO_2 + O_2, visible light; 4: AR/SiO_2/TEMPO + O_2, visible light; 5: TiO_2/TEMPO + O_2, visible light; 6: AR + O_2, visible light; 7: TEMPO + O_2, visible light; 8: AR/TiO_2/TEMPO + Ar, visible light; 9: AR/TiO_2/TEMPO + O_2, visible light. In each experiment the 8 mg of the AR/TiO_2 photocatalyst was used (which contained 6.5×10^{-4} mmol AR); 2×10^{-3} mmol TEMPO and 0.1 MPa O_2 were used (if they are listed).

To verify the hypothesis, we used the commercial anthraquinone dye Alizarin Red (AR) as the sensitizer and TEMPO as the cocatalyst in a a suspension of TiO_2 in benzotrifluoride (BTF). BTF was chosen as solvent because of its inertness to oxidation and high solubility for dioxygen. AR was chosen because of its high extinction coefficient ($\varepsilon_{max}\approx 28000$) at wavelengths of 400–500 nm in the visible region and its redox potential which is suitable for effectively driving the corresponding events of electron transfer from the excited state of AR to the conduction band of TiO_2 and from TEMPO to the dye radical. The redox potential $E^0_{AR*/AR^{+\bullet}}$ (−1.57 V vs. standard hydrogen electrode, SHE) is lower than E_{cb} of TiO_2 (−0.50 V vs. SHE), and $E^0_{AR^{+\bullet}/AR}$ (0.79 V vs. SHE) is higher than $E^0_{TEMPO/TEMPO^+}$ (0.64 V vs. SHE) (see Table S2 in the Supporting Information).[8] Moreover, AR can be strongly preanchored on the TiO_2 surface by coordination of the SO_3^- group to the surface sites of TiO_2. AR/TiO_2 hardly dissociates into the solution during the photoreaction, so that it can be easily recovered by filtration for reuse (see Figure S1 in the Supporting Information). In control experiments (Figure 1), we found no obvious transformation of benzyl alcohol in the absence of anyone of TiO_2, dye, or dioxygen. The reaction could not take place without visible-light irradiation. Alcohols could also be transferred in this system under UV irradiation. However, in this case, not only the dye but also TiO_2 was excited by UV light and holes were produced, which led to uncontrollable deep oxidations and low selectivity.[9] When TiO_2 was replaced with SiO_2 nanoparticles, the reaction did not occur; this indicates that the process of electron injection from the excited state of the dye to the conduction band of TiO_2 is important. Benzyl alcohol could also be oxidized by dye/TiO_2 under visible-light irradiation in the absence of TEMPO (Figure 1, experiment 3); however, the reaction was much slower and the AR degraded quickly. This is in agreement with the sensitization degradation of dyes by TiO_2 in the presence of dioxygen.[7] The AR/TiO_2/TEMPO triad system exhibited remarkable reactivity and selectivity for transformation alcohols in the presence of O_2 under visible-light irradiation ($\lambda > 450$ nm) (Figure 1, experiment 9). The turnover number (TON) is over 100, indicating that this is a catalytic reaction. However, these TON values are low compared to those reported for other oxidation systems. The photonic efficiency is also relatively low for this reaction (0.2% at 525 nm, for the transformation of benzyl alcohol), suggesting that the system can be optimized in further studies.

The conversion, selectivity, and TON of the oxidation of a broad range of alcohols with the proposed system are summarized in Table 1. Of these substrates, aromatic alcohols such as *p*-methoxyl benzyl alcohol could be easily oxidized with high TON (154) and selectivity (99%, Table 1, entry 4), while aliphatic alcohols (entry 8) exhibited relatively low activity. It is worth noting that allylic alcohols could be oxidized to the corresponding α,β-unsaturated aldehydes with high selectivity (94–98%) without protection of the double bond (Table 1, entries 7 and 9). More interestingly, alcohols containing a N heteroatom, which are generally not reactive in transition-metal-catalyzed reactions,[10] could also be converted with high selectivity (Table 1, entry 10). However, the present system exhibits very low activity for the transformation of secondary cyclic alcohols (Table 1, entry 11) compared with the activity for primary alcohols. This is attributed to the inherent limitations of TEMPO.[3] The photocatalytic reaction could also be carried out on a larger scale. For instance, when the reaction in Table 1, entry 1, was conducted on a large scale, it still exhibited high activity (TON = 665) and selectivity (Table 1, entry 2). Thus, a visible-light-induced system to realize the selective oxidation of alcohols has been assembled successfully. In this system, all components—TiO_2, dye, TEMPO, dioxygen, and visible-light irradiation—make unique contributions. A broad range of alcohols were transformed with greater than 93% selectivity with this system; this selectivity is much higher than that in the TiO_2 photocatalytic oxidation under UV irradiation, especially for aliphatic alcohols.

Table 1: Aerobic oxidation of alcohols with the AR/TiO_2/TEMPO catalyst system under visible-light irradiation.[a]

Entry	Substrate	Product	t [h]	Conv. [%]	TON_{dye}[b]	Sel. [%]
1			18	80	123	98
2[c]			100	43	665	98
3			15	87	135	97
4			15	100	154	99
5			15	59	91	99
6			20	49	76	98
7			13	66	101	98
8			22	20	31	93
9[d]			16	71	218	94
10			10	23	36	95
11			16	7	10	99

[a] Reaction conditions: Alcohol (0.1 mmol), AR/TiO_2 (8 mg, containing 6.5×10^{-4} mmol AR), and TEMPO (2×10^{-3} mmol) were stirred in 1.5 mL of BTF under 0.1 MPa O_2 under visible-light irradiation ($\lambda > 450$ nm). [b] TON_{dye} was calculated as $n_{product}/n_{AR}$ [c] Scaled-up reaction: 5 mmol substrate, 40 mg AR/TiO_2, 0.01 mmol TEMPO in 30 mL BTF. [d] 0.2 mmol substrate..

The results of electron spin resonance (ESR) experiments (Figure 2) also support the photocatalytic cycles proposed in Scheme 2. For the sample containing only AR/TiO_2, a strong single peak at $g = 2.0067$ appeared upon laser irradiation at 532 nm which is attributed to the radical of AR. The AR radical is generated by electron injection from the excited state of AR to the conduction band of TiO_2.[8] When TEMPO was added to this system, a triplet peak at $g = 2.0079$ with a splitting constant of $a_N = 16.8$ G was observed before the sample was irradiated. This triplet peak was assigned to the free radical TEMPO. Upon laser irradiation at 532 nm, the intensity of the triplet peak decreased immediately, and the single peak of the AR radical appeared. These changes in the ESR signals correspond to the oxidation of TEMPO to $TEMPO^+$ by the AR radical. The broader single peak of the AR radical can be explained by the interaction existing between the two types of radicals.[11] The intensity of the triplet peak of TEMPO remained at a certain level, suggesting that TEMPO is in the catalytic cycle.

The catalytic cycle involves two important steps of electron transfer: 1) the electron injection from the excited dye molecule to the conduction band of TiO_2 to generate dye radical; and 2) the dye-radical-promoted oxidation of TEMPO to $TEMPO^+$, which can selectively oxidize the alcohols to aldehydes. Dioxygen reacts with e_{cb}^- to form $O_2^{\bullet -}$ (which reacts further to give H_2O_2 or H_2O) and enables the excited state of the dye molecules to inject electrons into the conduction band of TiO_2 incessantly.[7,8] The byproduct H_2O_2 produced by the trapping of e_{cb}^- by dioxygen was also detected by idiometric titration method (see Table S1 in the Supporting Information).

In summary, the selective oxidation of alcohols was achieved under visible-light irradiation in a system containing dye-sensitized TiO_2 and TEMPO. This photocatalytic system employs neither transition-metal ions nor deleterious oxidants such as Br_2 and NO_2^-. The reaction is driven by visible-light irradiation at ambient temperature and uses molecular oxygen as the oxidation agent. It exhibits very good selectivity because the process does not generate holes in valence band of TiO_2. Our work indicates that the photocatalytic synthesis of many fine chemicals can potentially be achieved with high product selectivity when the catalysis systems are properly assembled.

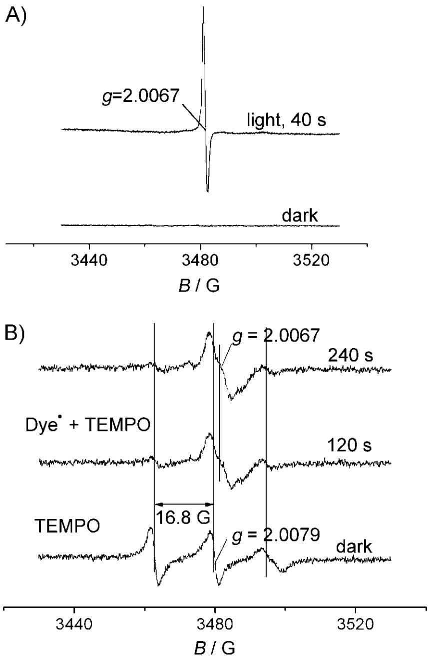


Figure 2. A) The ESR spectrum of the cation radical of AR•. AR/TiO_2 (8 mg, containing 6.5×10^{-4} mmol AR) in benzotrifluoride (BTF) (0.5 mL) was stirred and then put into a quartz tube. B) Changes in the ESR spectra of TEMPO and AR•. TEMPO (1×10^{-6} M), AR/TiO_2 (8 mg, containing 6.5×10^{-4} mmol AR), and benzyl alcohol (0.1 mmol) were added to BTF (0.5 mL). The mixture was stirred and then put into a quartz tube. In situ irradiation from a laser (532 nm) was used in this experiment.

Experimental Section

Oxidation of alcohols: A mixture of the alcohol (0.1 mmol), AR/TiO$_2$ (8 mg, containing 6.5×10^{-4} mmol AR), and TEMPO (0.002 mmol) in benzotrifluoride (BTF) (1.5 mL) was transferred into a 10 mL Pyrex bottle. The container was filled with pure oxygen at a pressure of 0.1 MPa. The mixture was stirred under irradiation from a 500 W halogen lamp with a light filter to cut off light of wavelength <450 nm. After the reaction, the reaction mixture was filtered through a membrane with pore diameter of 20 μm and then analyzed with a HITACHI Gas Chromatograph (GC 3900). The structures of the products were confirmed by comparison with standard samples and by GC-MS (Thermo-Finingan; Trace 2000/Trace DSQ).

ESR experiments were conducted with a Bruker EPR ELEXSYS 500 spectrometer equipped with an in situ irradiation source (a Quanta-Ray Nd:YAG laser system with $\lambda = 532$ nm). The same quartz tube was used for all the measurements to minimize errors.

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