VIP Heterogeneous Catalysis

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Photocatalytic Aerobic Oxidation of Alcohols on TiO_2: The Acceleration Effect of a Brønsted Acid**

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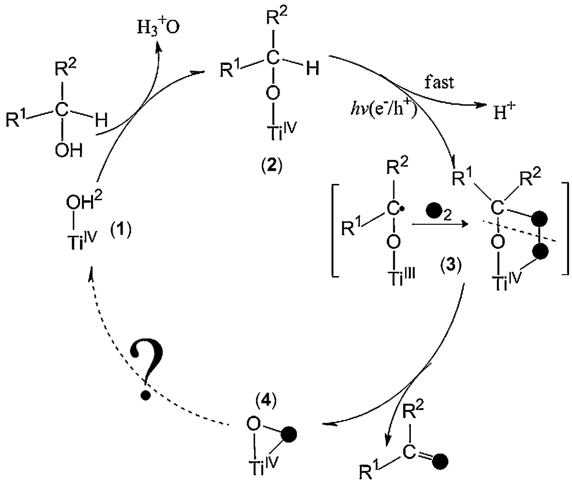
The selective oxidation of alcohols into carbonyl compounds is one of the most important reactions in both the industrial synthesis of fine chemicals and laboratory research.[1–3] The search for green and economic reaction systems that avoid using corrosive chemical oxidants such as ClO^-, Cr^{VI}, Cl_2, and peroxy acids, high concentrations of bases media, and dissolved transition-metal catalysts has attracted great attention. TiO_2 photocatalysis, which can readily initiate oxidation of nearly all organic substrates by using molecular oxygen as ultimate oxidant, is highlighted and widely used for decontamination of water and air.[4] Recently, a few successful cases involving TiO_2 photocatalysis in water and organic solvents have been reported as a new and promising route for selective oxidation of organic compunds.[5–6] However, unlike the accepted explanation of the nonselectivity of oxidation by OH radicals as well as auto-oxidation in the photocatalytic degradation of organic pollutants,[4] the detailed photocatalytic mechanism for the selective oxidation of organic compounds is unclear, and the slow reaction rates still remain a challenge.



Scheme 1. The proposed reaction cycles in the TiO_2 photocatalytic oxidation of alcohols. ●: oxygen atom originating from dioxygen.

Very recently, we found an unexpected oxygen atom transfer from molecular oxygen to alcohols during the TiO_2 photocatalytic oxidation of alcohols in a benzotrifluoride solvent, and the Ti intermediate **4** with a side-on peroxide (Scheme 1) was characterized by ^{18}O-labeling experiments.[7] In oxidative transformations of alcohols in most other systems, nearly all the product aldehydes/ketones contain the same alkoxy oxygen atom that was in the starting alcohol,[2] however, in the TiO_2 photocatalysis a unique mechanism in which an intermediate derived from a nascent ring addition of a carbon-centered radical and dissolved dioxygen (see **3**, Scheme 1), predominates. This mechanism motivated us to revisit the capability of TiO_2 photocatalysis in selective transformation of organic chemicals. Herein we report a crucial finding: the photocatalytic oxidation of alcohols on TiO_2 could be dramatically accelerated without any loss of selectivity by simple adsorption of a Brønsted acid, and a two-fold conversion was achieved when a small quantity of SiO_2 was incorporated into TiO_2—after the pretreatment with acid—to afford more Brønsted acid sites. These results are significantly different from those obtained from noble- or transition-metal catalysis systems in which a high concentration of base (>20 mol%) is usually required.[3a–c] This effect results from the decomposition of the relatively stable side-on peroxide promoted by the protons of Brønsted acids, which effectively clean the catalytic $Ti\text{-}OH_2$ sites. This finding not only strengthens the fundamental insight into the photocatalysis mechanism for the selective oxidation reactions, but also opens a new path to obtaining both high selectivity and conversion in TiO_2 photocatalysis.

TiO_2 and SiO_2/TiO_2 (7% Si/Ti) were prepared using a sol-gel method through the hydrolysis of titanium(IV) *n*-butoxide and subsequent sintering at 430 °C (anatase type). The prepared TiO_2 photocatalysts were then pretreated with different Brønsted acids (for details see the Supporting Information) and their photocatalytic activities for benzyl alcohol oxidation are summarized in Table 1. In a typical reaction, the photocatalyst (25 mg) and alcohol (0.1 mmol) were added to benzotrifluoride (1.5 mL), and then the reaction mixture was purged with O_2 (0.1 MPa) and irradiated by UV light at room temperature. Surface modification of TiO_2 with both inorganic and organic acids significantly accelerated the conversion of the alcohol (Table 1, entries 2–8) without any loss of selectivity relative to the control (Table 1, entry 1). By contrast with conventional noble- or transition-metal catalysis,[3a–c] pretreatment with a base had

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Table 1: Aerobic oxidation of benzyl alcohol to benzaldehyde by TiO_2 and Si/Ti photocatalysts pretreated with various acids, bases, and salts.

Entry	Modifier (1 M)	Conv. [%] (TiO_2)	Conv. [%] (Si/Ti)
1	None	42	46
2	HF	66	91
3	HCl	72	89
4	H_3PO_4	72	80
5	H_2SO_4	62	90
6	$HClO_4$	57	73
7	HNO_3	60	89
8	CF_3COOH	70	82
9	NaOH	43	50
10	Pyridine	40	42
11	Et_3N	44	45
12	NaF	46	42
13	$NaNO_3$	42	46
14	NaCl	46	50
15	Na_2SO_4	43	49

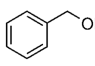
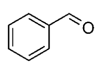
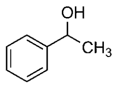
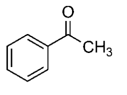
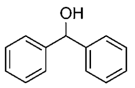
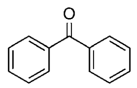
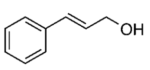
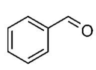
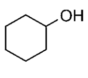
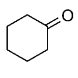
Reaction conditions: benzyl alcohol (0.1 mmol), photocatalyst (25 mg), benzotrifluoride (1.5 mL), 0.1 MPa O_2, 4 h UV irradiation. Light source: 100 W Hg-lamp. The selectivity of benzaldehyde exceeded 95 % in all the cases except for the TiO_2 and Si/Ti, pretreated with HNO_3 (entry 7), wherein the selectivity of benzaldehyde was 80% and 85 %, respectively. The catalyst (TiO_2 or Si/Ti) was pretreated with aqueous solutions of different modifiers (0.5 g catalyst/5 mL, 1 M modifiers except H_2SO_4 (entry 5: 0.5 M)), separated by centrifugation and then dried (see procedure 1 in the Supporting Information). After the reaction, the products were analyzed by GC and GC/MS after separation of the catalyst particles by centrifugation.

negligible effect in the present system (Table 1, entries 9–11), indicating that β-hydride elimination, the well known rate-determining step in the traditional catalytic oxidation of alcohols,[8] does not occur or becomes a non-rate-determining step in the TiO_2 photocatalytic transformation. In contrast, the salts containing the corresponding counter anions in all the above acids showed little effect upon the photooxidation of benzyl alcohol (Table 1, entries 12–15), thereby illustrating that the enhanced reactivity exclusively originates from the protons rather than the counter anions. Moreover, once the photocatalysts, pretreated with a Brønsted acid, were washed with distilled water and dried again in vacuum, the accelerating effect was no longer observed, therefore indicating that the protons are simply adsorbed onto the TiO_2 surface. Accordingly, direct addition of Brønsted acids into the reaction dispersions containing the photocatalyst should have a similar effect compared to that of the pretreated catalyst. As expected, a similar acceleration was observed in the photooxidation of benzyl alcohol on TiO_2 when the Brønsted acid was directly added to the reaction mixture (see Figure S1 in the Supporting Information). In the present system, the protons are adsorbed completely upon the surface of the TiO_2 and do not dissolve in the organic solvent (see Table S1 in the Supporting Information). All of the results clearly reveal very important features: 1) the simple adsorption of Brønsted acids significantly accelerates the oxidative transformation of alcohols, which provides an approach to address the of low efficiency in TiO_2 photocatalytic synthesis on large scale; 2) the high concentration of base in solutions used for common homogeneous transition-metal catalysis is no longer required in the case of TiO_2 photocatalysis, instead, only a simple and separable solid catalyst having an adsorbed Brønsted acid is sufficient.

The effective sites for adsorption of a Brønsted acid are well-defined for the pure TiO_2 photocatalyst (anatase, see below). To obtain more sites, we prepared Si/Ti that was determined to have more active sites for adsorption of the Brønsted acid.[9] Indeed, the Si/Ti photocatalyst, after acid pretreatment, always showed much greater conversion than the pure TiO_2 (Table 1, entries 2—8). The net increase in the conversion resulting from the SiO_2 modification prior to the Brønsted acid pretreatment was not significant (Table 1, entry 1, 42 % versus 46 % conversion), but the incorporation of SiO_2 into TiO_2 creates additional sites for adsorbing more of the Brønsted acid and thus leads to much greater activity (Table 1, entry 2, 66 % and 91 % conversions for HF-pretreated TiO_2 and HF-pretreated Si/Ti, respectively). Therefore, it is the Brønsted acid rather than the Si/Ti sites that accelerate the oxidation of alcohols.

To demonstrate the universality of effect of the protons upon oxidation, HF was chosen as model acid to pretreat TiO_2 and Si/Ti since the F^- ion itself is redox inert and cannot generate any reactive radicals under UV illumination ($E^0_{F^-/F^\cdot} = 3.6$ V vs NHE; NHE = normal hydrogen electrode). The results of the photocatalytic oxidation of different alcohols by HF-pretreated or untreated TiO_2 and Si/Ti are summarized in Table 2. Clearly, the pretreated TiO_2 and Si/Ti significantly promoted the conversion of all the tested alcohols relative to the untreated catalysts. In the transformation of all the alcohols except dibenzylmethanol (Table 2, entry 3; 48 % versus 58 % conversion for TiO_2 and Si/Ti, respectively), the Si/Ti catalyst without the Brønsted

Table 2: Photocatalytic aerobic oxidation of various alcohols on pretreated and untreated TiO_2 and Si/Ti at room temperature.

Entry	Substrate	Product	t [h]	Catalyst[a]	Conv. [%]	Sel. [%]
1			4	TiO_2	42	98
				H^+/TiO_2	66	99
				Si/Ti	46	98
				H^+/Si/Ti	91	100
2			6	TiO_2	34	92
				H^+/TiO_2	57	95
				Si/Ti	40	93
				H^+/Si/Ti	95	98
3			7	TiO_2	48	89
				H^+/TiO_2	65	90
				Si/Ti	58	90
				H^+/Si/Ti	100	93
4			2	TiO_2	33	80
				H^+/TiO_2	60	74
				Si/Ti	35	73
				H^+/Si/Ti	100	87
5			5	TiO_2	42	93
				H^+/TiO_2	56	96
				Si/Ti	44	92
				H^+/Si/Ti	85	93

Reaction conditions: substrates (0.1 mmol), photocatalyst (25 mg), benzotrifluoride (1.5 mL), 0.1 MPa O_2. [a] H^+: TiO_2 and Si/Ti were pretreated with 1 M hydrofluoric acid according to the same procedure described in Table 1. After the reaction, the products were analyzed by GC and GC/MS after separation of the catalyst particles by centrifugation.

acid exhibited an insignificant acceleration effect compared to that of pure TiO_2. However, about one or two times higher conversions were obtained in the transformation of all the substrates after pretreatment of the catalyst with a Brønsted acid, thus validating the significant promotion effect of Brønsted acids. Additionally, such an acceleration effect does not result in poorer selectivity, suggesting that the oxidation process on the surface of the pretreated TiO_2 and Si/Ti catalysts should proceed by the proposed mechanism (Scheme 1) rather than the traditional photocatalytic pathways of nonselective OH radicals and radical auto-oxidation in the presence of O_2.

The detailed dynamic experiments were carried out to examine the effect of H^+. Herein, the commercial P25 TiO_2 was used as photocatalyst. When the amounts of catalyst and substrate were fixed, the activity increased initially with an increase in the amount of H_2SO_4 added. After reaching a maximum at 1.0 mmol H^+/gTiO_2, the activity decreased gradually as the amount of acid was increased (see Figure S1 in the supporting Information). The optimal amount of acid was changeless when initial concentration of substrate was varied at given amount of TiO_2 (see Figure S2 in the Supporting Information). In the transformation of benzyl alcohol, the turn-over number per proton reached approximately 9.6 without decrease of conversion rate, suggesting that the behavior of additional protons is catalytic rather than consumptive. Moreover, an intermediate species having a yellow color on the TiO_2 surface was observed after the photoreaction, and it was detected by using UV/vis diffuse reflection absorption spectra. There is a significant difference between the TiO_2 catalysts pretreated with the Brønsted acid and the untreated catalysts, as characterized by their spectra (see Figure S3 in the Supporting Information). The intermediate species formed easily and accumulated upon the untreated TiO_2, whereas this species on the pretreated TiO_2 was reduced significantly and could be observed only after many runs of the repeated photoreactions. Therefore, the Brønsted acid adsorbed onto the photocatalyst, in a sense, plays the role of regenerating the catalyst surface sites through timely removal of the intermediate species from the surface. Next we attempted to identify the intermediate that accumulated on the surface of TiO_2 photocatalyst during the reaction and determine why it was readily eliminated by the acid, H^+.

In previous work,[7] we evidenced the generation of a Ti intermediate, with a side-on peroxide, by using ^{18}O labeling and Raman spectroscopy. Its decomposition may involve the protons. To exclusively study the decomposition properties by using spectroscopy to monitor titration experiments, we prepared a defined Ti species, with a side-on peroxide, on the TiO_2 particles in relatively large quantities in the absence of the organic substrates. These specially prepared particles would also avoid the difficult identification of relatively weak signals of the side-on peroxide in the Raman spectra, as well as possible interference of in situ produced organic peroxides. The prepared TiO_2 (anatase) was firstly mixed with H_2O_2 to form a yellow TiO_2/peroxide complex and subsequently washed with water three times to remove physically adsorbed H_2O_2 and produced protons. The mixture was then separated by centrifugation and dried under vacuum at room temperature. The as-prepared yellow surface complex (denoted as H_2O_2/TiO_2 with $\lambda_{max} \approx 410$ nm, Figure 1 A, dashed line), the pattern and characteristics of which were in good agreement with those reported before[10a] and those of the surface intermediate species generated in the transformation of alcohols mentioned above (see Figure S3 in the Supporting Information), was already confirmed as the side-on peroxide structure **4**.[10b] This colored side-on peroxide was very stable for a period of 12 hours and even after drying again at 70 °C. Its decomposition was relatively slow, even upon UV irradiation when no Brønsted acid was added (Figure 1 b). Although the wavelength of maximum absorption for the surface complex red-shifted to $\lambda_{max} \approx 421$ nm after addition of

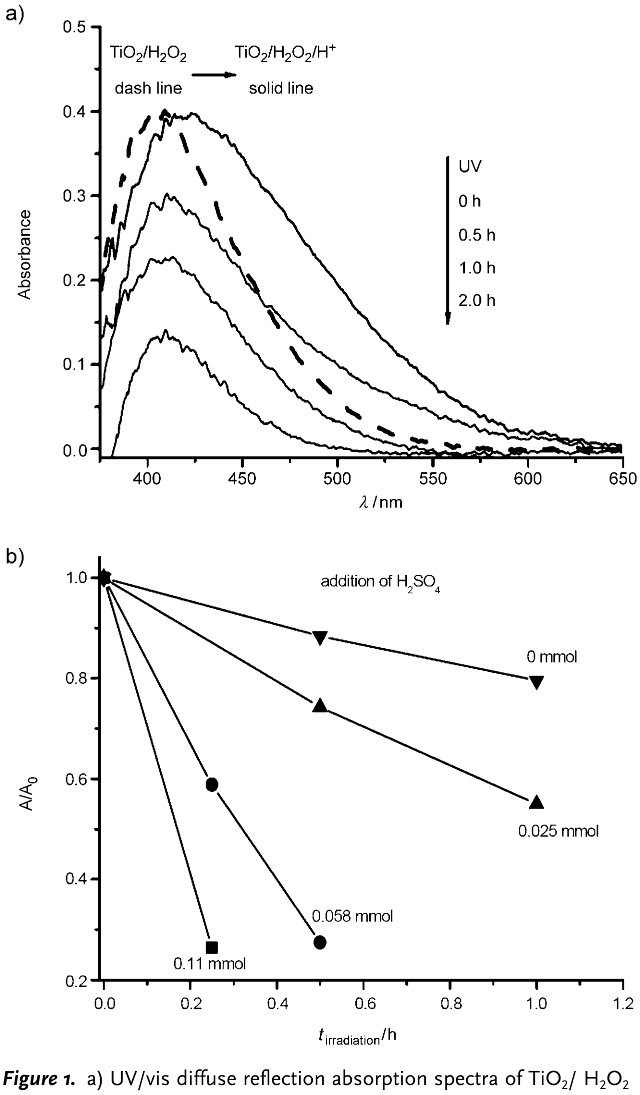
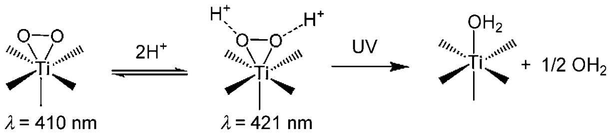


Figure 1. a) UV/vis diffuse reflection absorption spectra of TiO_2/ H_2O_2 samples before (dashed line) and after addition of 0.025 mmol acid ($TiO_2/H_2O_2/H^+$; solid line). The spectral changes of $TiO_2/H_2O_2/H^+$ at different UV irradiation intervals are also shown. b) The absorption changes of TiO_2/H_2O_2 as a function of UV irradiation time in the absence and presence of different amounts of H^+. Reaction conditions: 0.1 g dry TiO_2/H_2O_2 samples were suspended in 2 mL benzotrifluoride and concentrated sulfur acid (98%) was directly added to the system.

the Brønsted acid, probably because of the intense protonation of the side-on peroxide, the peak intensity did not change before UV irradiation (Figure 1 a), but gradually decreased under UV irradiation. The decomposition dynamics at the surface of the Ti/peroxide species after addition of different amounts of Brønsted acid under UV irradiation is shown in Figure 1 b. The spectra obtained from the titration results clearly demonstrate that the adsorbed protons are responsible for promoting the photodecomposition of the side-on peroxide; the greater the amounts of the adsorbed protons, the faster the peroxide degrades when the amount of adsorbed protons is below the optical value. Similar phenomena were also observed in the case of the Si/Ti photocatalyst.

Theoretically, the decomposition of side-on peroxide by heterolysis of the O–O bond will be facilitated by the adsorbed protons because the protonation of peroxide remarkably weakens the O–O bond.[11] Since neither the $^{\bullet}$OH radical production nor the auto-oxidation that frequently decreases the reaction selectivity were observed in the reaction[7] we conclude that the role of proton is mainly to accelerate the disproportionate decomposition of the side-on peroxide as shown below:



In summary, this study showed for the first time that the simple pretreatment of TiO_2 and Si/Ti with Brønsted acids can lead to significant rate enhancement for the oxidation of alcohols without any loss of selectivity when compared to the results of using the untreated TiO_2. Such a unique effect of protons n the reaction is attributed to the promotion of decomposition of the surface Ti/peroxide species and regeneration of Ti sites in the photocatalytic transformation of alcohols.

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