Green Chemistry

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Solvent-free selective photocatalytic oxidation of benzyl alcohol over modified TiO$_2$

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Heterogeneous photocatalysis offers a promising route to realize green oxidation processes in organic synthesis. In this research, the solvent-free selective photocatalytic oxidation of benzyl alcohol to benzaldehyde in the presence molecular oxygen was studied by using TiO$_2$ and modified TiO$_2$ as photocatalysts. The surface modification of TiO$_2$ by transition metal clusters dramatically enhanced the photocatalytic oxidation activity. Ir/TiO$_2$ prepared by photodeposition showed a remarkably high activity for the photocatalytic oxidation of benzyl alcohol, and an average reaction rate of 14538 µmol h^{-1} g$_{cat}$$^{-1}$ could be obtained. The effect of preparation method, iridium loading and reaction conditions on the catalytic performance of Ir/TiO$_2$ is investigated in detail. Based on the catalytic and characterization results, the problem of product selectivity and the reaction mechanism of the photocatalytic oxidation of benzyl alcohol over Ir/TiO$_2$ are discussed.

Introduction

The selective oxidation of alcohols to carbonyl compounds is one of the most important organic transformations, which is of great interest not only to fundamental organic synthesis but also to the fine chemical industry.[1,2] Conventionally, stoichiometric oxidants, *e.g.* dichromate and permanganate, are employed in the process of alcohol oxidation. These oxidants are usually toxic and/or expensive, and large amounts of waste are produced together with the desired products. To address this concern, it has been proposed to use molecular oxygen as a clean and cheap oxidant to realize a so-called green oxidation process.[3] Numerous catalyst systems, *e.g.* Au[4–6] and Pd[7–9] catalysts, have been developed for the selective oxidation of alcohols with molecular oxygen as the oxidant.

Heterogeneous photocatalysis, which has been known since the 1970s, has drawn great attention in past decades. In heterogeneous photocatalysis, holes in the valence band and electrons in the conducting band are created when the semiconductor is illuminated by photons of energy higher than its band gap. Since the valence holes are powerful oxidants, they have been extensively used in the degradation of organic pollutants.[10,11] Recently, the application of heterogeneous photocatalysis in organic synthesis, *e.g.* most commonly in selective oxidation, has been highlighted.[12–14] Generally, heterogeneous photocatalytic oxidation reactions are performed under mild reaction

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conditions, and oxygen is involved in the reaction instead of toxic and corrosive oxidants. Therefore, heterogeneous photocatalysis offers an alternative green oxidation process. Although the efficiency of heterogeneous photocatalysis is not as high as conventional heterogeneous catalysis (non-photocatalysis), heterogeneous photocatalysis still attracts great attention for its chemical utilization of solar energy. Heterogeneous catalysis is considered to be green chemistry with minimal environmental impact. TiO$_2$ is a well known and applicable semiconductor photocatalyst due to its chemical and physical durability, non-toxicity and commercial availability.[15] Up to now, TiO$_2$ has been employed as a possible catalyst in various selective photocatalytic oxidation reactions under different conditions.[16–22] In the work of Mohamed *et al.*, anatase TiO$_2$ was employed in the photocatalytic oxidation of 1-phenylethanol in dry acetonitrile under UV irradiation, and the rate-determining step was hypothesized to be the reaction between the superoxide and the alcohol radical cation over the surface.[16] Palmisano *et al.* prepared rutile TiO$_2$ at low temperature and employed it in the photocatalytic oxidation of aromatic alcohols to aldehydes in water suspensions under UV irradiation. The crystallinity of the sample appeared to be a key factor controlling the product selectivity,[17] while the introduction of substituents into the aromatic alcohols also changed the photocatalytic oxidation rate and product selectivity.[18] More recently, Higashimoto *et al.* reported that the photocatalytic oxidation of benzyl alcohol and its derivatives into the corresponding aldehydes could be achieved over TiO$_2$ in acetonitrile under the irradiation of both UV and visible light.[19,20] The visible light response of TiO$_2$ was attributed to the characteristic surface complex formed by the adsorption of the benzyl alcoholic compound on the TiO$_2$ surface.[19]

Despite the significant research on selective photocatalytic oxidation reactions, several very important issues remain to be solved. First of all, the rates of most photocatalytic oxidation reactions are very low and far from sufficient for practical applications. Moreover, the photogenerated holes formed in photocatalytic oxidation processes have a high oxidative potential and may oxidize organic species indiscriminately, leading to poor product selectivity.[24] For an ideal green oxidation process, an environmentally benign catalyst with a high activity and selectivity should be involved. Meanwhile, the oxidation reaction should be performed under mild conditions and be free of solvents or additives. However, with a few exceptions,[25,26] most selective photocatalytic oxidation reactions are performed in water suspensions or even in organic solvents.

In the present study, a series of transition metal-modified TiO_2 materials are examined as photocatalysts for the solvent-free selective oxidation of benzyl alcohol. The newly-developed Ir/TiO_2 catalyst appears to be a promising choice to realize selective photocatalytic oxidation processes. Based on the comprehensive physicochemical characterization of Ir/TiO_2, the modification effects of iridium on TiO_2 are discussed and the mechanism of the photocatalytic oxidation is proposed.

Experimental methods

Preparation of M/TiO$_2$ catalyst

Commercial TiO_2 (Degussa P25, 70% anatase, 30% rutile) was used as a support and M/TiO_2 (M = Ag, Au, Pd, Pt and Ir) catalysts were prepared by the so-called photodeposition method.[27,28] In a typical synthesis of Ir/TiO_2, a certain amount of a 2 mM H_2IrCl_6 solution, 500 mg of TiO_2 and 10 mL of ethanol were added into a round-bottomed quartz flask under vigorous stirring to form a slurry. The slurry was adjusted to pH 11 ± 0.5 using either a 1 M HCl or a 1 M NaOH aqueous solution and irradiated by a high pressure mercury light with a main wavelength of 365 nm for 6 h under the protection of nitrogen. After irradiation, the particles were filtered, dried under ambient conditions, reduced by 5 vol% H_2/Ar at 573 K for 2 h and denoted as Ir/TiO_2-p. Ir/TiO_2 samples with similar Ir loadings were also prepared by the wet impregnation and chemical reduction method. For wet impregnation, 50 mL of a 2 mM H_2IrCl_6 solution was added to 500 mg of TiO_2, and then the mixture was evaporated in a rotary evaporator at a constant temperature of 353 K. The as-obtained particles were carefully washed with de-ionized water, dried under ambient conditions, reduced by 5 vol% H_2/Ar at 573 K for 2 h and denoted as Ir/TiO_2-i. For chemical reduction, 500 mg of TiO_2 and 50 mL of a 2 mM H_2IrCl_6 solution were added into a round-bottomed quartz flask under stirring to form a slurry. Then, 10 mL of a 1 M KBH_4 solution was dropwise added to the slurry under the protection of nitrogen. The particles were filtered, washed with de-ionized water and dried under ambient conditions. After reduction by 5 vol% H_2/Ar at 573 K for 2 h, the product was denoted as Ir/TiO_2-c.

Bimetallic $Pd-Ir/TiO_2$ was prepared by the co-instantaneous photodeposition process, and a mixture of H_2IrCl_6 and $PdCl_2$ solution was used for the photodeposition instead of a H_2IrCl_6 solution. After reduction post-treatment, the sample was de-

noted as $Pd-Ir/TiO_2$-p. Bimetallic $Pd-Ir/TiO_2$ samples were also prepared by the co-instantaneous wet impregnation and chemical reduction method. The final products were denoted as $Pd-Ir/TiO_2$-i and $Pd-Ir/TiO_2$-c, respectively.

Sample characterization

Transmission electron microscopy (TEM) images of samples were acquired by a Tecnai G^2 2010 S-TWIN transmission electron microscope at an accelerating voltage of 200 kV.

Diffuse reflectance ultraviolet-visible (UV-vis) spectra were recorded in air against $BaSO_4$ in the region 200–700 nm on a Varian Cary 300 UV-vis spectrophotometer.

Photoluminescence (PL) spectra were recorded on a Spex FL201 fluorescence spectrophotometer. Samples were dry-pressed into self-supporting wafers and then illuminated by a 325 nm He-Cd laser as the excitation source at ambient temperature.

X-Ray photoelectron spectra (XPS) of samples were recorded on a Kratos Axis Ultra DLD spectrometer with a pass energy of 20 eV and a monochromated Al-Kα X-ray source. Accurate binding energies (±0.1 eV) were determined with respect to the position of the adventitious C 1 s peak at 284.8 eV.

Photocatalytic oxidation of benzyl alcohol

The catalytic oxidation of benzyl alcohol was performed in a double-walled quartz cell cooled by water with a 250 W high pressure Hg lamp (315–420 nm, main wavelength at 365 nm) as the light source. In each experiment, *ca.* 0.3 g catalyst was dispersed in 0.3 mol benzyl alcohol in a quartz cell under stirring. The suspension was then irradiated from inside, with oxygen bubbled in at *ca.* 20 mL min^{-1}. The organic products were analyzed by GC (Shimadzu GC-2010 Plus) and GC-MS (Shimadzu GCMS-QP2010 SE). Meanwhile, an absorption apparatus containing a saturated $Ba(OH)_2$ solution was equipped downstream of the quartz cell to determine the quantity of CO_2 that might have formed during the reaction.

Results and discussion

Photocatalytic oxidation of benzyl alcohol over M/TiO$_2$

The results of the selective photocatalytic oxidation of benzyl alcohol over TiO_2 and modified TiO_2 are shown in Table 1. No detectable oxidation reaction took place under irradiation without catalyst, and therefore the homogeneous photochemical oxidation contribution will be neglected in further discussions. TiO_2 exhibits a very low activity in the photocatalytic oxidation of benzyl alcohol, with a reaction rate of 325 µmol h^{-1} g$_{cat}$$^{-1}$. The main oxidation products are carbonyl compounds (benzaldehyde, benzoic acid and benzylbenzoate), while small amounts of CO_2 and other unknown products could be detected. To enhance the photocatalytic activity of TiO_2, a series of transition metals were deposited on the surface. As expected, certain noble metals show dramatic promotion effects on the photocatalytic oxidation reaction. The work function of noble metals are higher than that of TiO_2, and the photogenerated electrons tend to migrate from TiO_2 to metal clusters and be trapped therein. In such a way, the deposition of metal clusters

Table 1 Selective photocatalytic oxidation of benzyl alcohol over modified TiO_2[a]

Catalyst	Metal loading[b] (%)	Metal size[c]/nm	Work function[d]	Conversion (%)	Product selectivity (%)			Reaction rate[g]/ μmol h^{-1} g$_{cat}$$^{-1}$
					Benzaldehyde	Carbonyls[e]	Others[f]	
TiO_2	/	/	/	0.2	50	92	8	325
Ag/TiO_2-p	3.5	2.8	4.26	2.4	81	97	3	3925
Au/TiO_2-p	3.6	5.7	5.1	6.4	81	98	2	10475
Pt/TiO_2-p	2.8	3.6	5.12	3.3	79	99	1	5363
Pd/TiO_2-p	2.8	3.3	5.65	4.1	81	98	2	6688
Rh/TiO_2-p	3.2	3.1	4.98	8.7	83	96	4	14012
Ir/TiO_2-p	3.5	2.9	5.27	8.9	92	99	1	14538
Ir/TiO_2-p[h]	3.5	2.9	5.27	0	/	/	/	0

[a] Reaction conditions: catalyst 0.3 g, benzyl alcohol 0.3 mol, reaction T 333 K, reaction time 6 h. [b] Analyzed by ICP. [c] Average size observed by TEM. [d] Work function of modified metals, data from ref. 29. [e] Including benzaldehyde, benzoic acid and benzylbenzoate. [f] Including CO_2 and other unknown products. [g] Rate of benzyl alcohol oxidation per unit of M/TiO_2 catalyst per unit time. [h] Without irradiation.

on the surface of TiO_2 can promote the separation of photogenerated electron–hole pairs and thus enhance the photocatalytic activity of TiO_2. Meanwhile, the deposition of noble metal clusters on the TiO_2 surface may facilitate the adsorption and activation of oxygen, which is good for the involvement of molecular oxygen in photocatalytic oxidation processes. Among all the M/TiO_2 photocatalysts studied, Ir/TiO_2, a rarely-studied example, exhibits the best catalytic performance with a high reaction rate of 14538 μmol h^{-1} g$_{cat}$$^{-1}$ (more than 40 times higher than TiO_2) being obtainable. No oxidation reaction took place without irradiation, proving that all the products are derived from the photocatalytic oxidation process. Ir/TiO_2 appears to be a very promising catalyst for the selective photocatalytic oxidation of benzyl alcohol, and therefore a detailed study on the modification effect of iridium on TiO_2 will be presented in the following section.

Photocatalytic oxidation of benzyl alcohol over Ir/TiO_2

It is generally acknowledged that the efficiency of metal modification on TiO_2 depends on the method to introduce metals and the physicochemical properties of the final materials.[30] In the present study, the usual methods, *e.g.* wet impregnation,

chemical reduction and photodeposition, were adopted for the preparation of Ir/TiO_2, and quite different results were obtained. As seen in Table 2, with similar iridium loadings, Ir/TiO_2 prepared by photodeposition (Ir/TiO_2-p) exhibited the highest photocatalytic activity, followed by Ir/TiO_2-i and then Ir/TiO_2-c. Photodeposition appears to be a more feasible method to introduce modifiers, consistent with literature reports.[27,31]

The TEM images of Ir/TiO_2 prepared by different methods are shown in Fig. 1, and it is seen that the iridium species tend to form small clusters on the surface of the TiO_2. Typically, homogeneous clusters of 2–4 nm, with an average size of 2.9 nm, are observed to evenly disperse on the TiO_2 support in Ir/TiO_2-p. Similarly, clusters of 1.5–4.5 nm, with an average size of 3.2 nm, are observed on the TiO_2 support in Ir/TiO_2-i. Meanwhile for Ir/TiO_2-c, larger non-uniform clusters of 2–6 nm are observed on the support.

Fig. 2 shows the diffuse reflectance UV-vis spectra of TiO_2 and Ir/TiO_2 prepared by the different methods. A strong absorption in the UV region, attributed to the band–band transition, is observed for TiO_2 P25. Besides the absorption in the UV region, obvious absorption in the visible range is observed in Ir/TiO_2-i and Ir/TiO_2-p, which should be related to oxygen vacancy formation and the gap states introduced by iridium

Table 2 Selective photocatalytic oxidation of benzyl alcohol over Ir/TiO_2[a]

Catalyst	Metal loading[b] (%)	Metal size[c]/nm	Reaction T/K	Conversion (%)	Product selectivity (%)			Reaction rate[f]/ μmol h^{-1} g$_{cat}$$^{-1}$
					Benzaldehyde	Carbonyls[d]	Others[e]	
Ir/TiO_2-i	3.8	3.2	333	4.5	89	98	2	7363
Ir/TiO_2-c	3.6	4.3	333	1.8	93	99	1	2925
Ir/TiO_2-p	3.5	2.9	333	8.9	92	99	1	14538
Ir/TiO_2-p[g]	3.5	2.9	333	6.1	93	99	1	14952
Ir/TiO_2-p[h]	3.5	2.9	333	11.5	90	99	1	14087
Ir/TiO_2-p	3.5	2.9	293	3.0	65	100	0	4851
Ir/TiO_2-p	3.5	2.9	313	4.2	80	99	1	6875
Ir/TiO_2-p	3.5	2.9	353	10.5	78	97	3	17203
Ir/TiO_2-p	0.7	2.2	333	5.5	96	99	1	9009
Ir/TiO_2-p	1.9	2.5	333	6.8	93	99	1	11138
Ir/TiO_2-p	6.6	3.7	333	3.6	92	98	2	5863

[a] General reaction conditions: catalyst 0.3 g, benzyl alcohol 0.3 mol, reaction time 6 h. [b] Analyzed by ICP. [c] Average size observed by TEM. [d] Including benzaldehyde, benzoic acid and benzylbenzoate. [e] Including CO_2 and other unknown products. [f] Rate of benzyl alcohol oxidation per unit of catalyst per unit time. [g] Catalyst 0.2 g, benzyl alcohol 0.3 mol, reaction time 6 h. [h] Catalyst 0.4 g, benzyl alcohol 0.3 mol, reaction time 6 h.
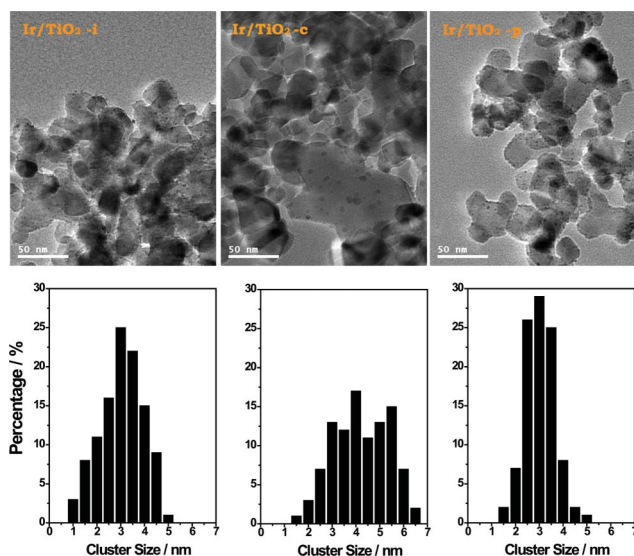
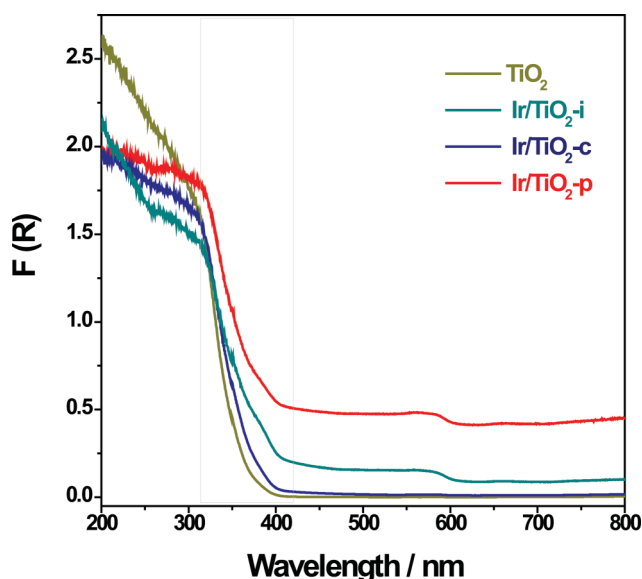**Fig. 1** TEM images and cluster size distributions of Ir/TiO$_2$ prepared by different methods.

Fig. 2 Diffuse reflectance UV-vis spectra of TiO$_2$ and Ir/TiO$_2$ prepared by different methods.

Fig. 3 PL spectra of TiO$_2$ and Ir/TiO$_2$ prepared by different methods.

modification. It should be mentioned that the light absorption of TiO$_2$ at 315–420 nm (wavelength of the high-pressure Hg lamp employed in the photocatalytic reaction) is enhanced by the iridium modification, and the order of the strength of absorption was observed to be Ir/TiO$_2$-p > Ir/TiO$_2$-i > Ir/TiO$_2$-c.

Photoluminescence spectroscopy is a very useful approach for disclosing the efficiency of charge carrier trapping, immigration and transfer in semiconductors. Generally, photoluminescence emission originates from the radiative recombination of photo-generated electrons and holes. The room temperature emission PL spectra of TiO$_2$ and Ir/TiO$_2$ prepared by the different methods are shown in Fig. 3. For TiO$_2$ P25, photoluminescence signals at wavelengths of 400–500 nm are observed. Typically, the signal at *ca.* 420 nm is attributed to the surface irradiative recombination, while the signal at *ca.* 460 nm is attributed to bulk irradiative recombination.[32,33] Both the photoluminescence
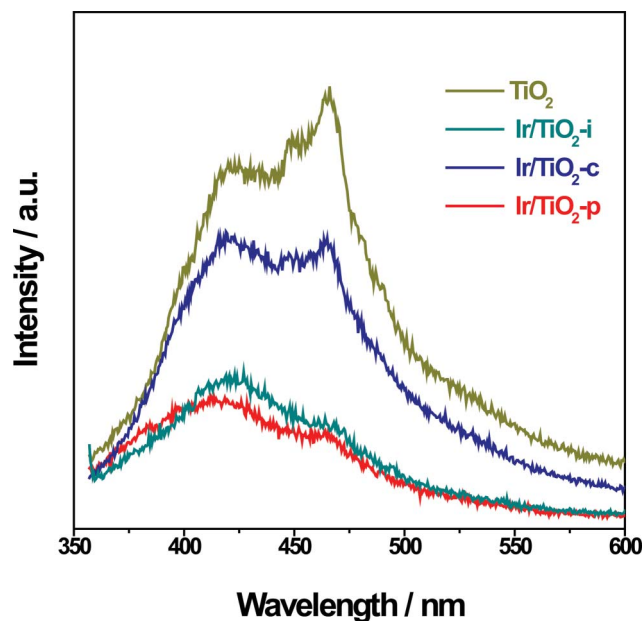
signals become much weaker with upon deposition of iridium on the TiO$_2$ surface, indicating that the iridium surface modification can suppress both surface and bulk irradiative recombination. This reasonably leads to a higher photocatalytic activity since the photocatalytic reaction is evoked by photogenerated electrons and holes. It is also observed that the different preparation methods of Ir/TiO$_2$ lead to different suppression effects for the recombination of photogenerated electrons and holes. The best suppression effect was obtained by Ir/TiO$_2$ prepared by photodeposition, followed by Ir/TiO$_2$-i and then Ir/TiO$_2$-c. Based on the results of the UV-vis and PL spectra, we conclude that the surface modification of TiO$_2$ by iridium can change the properties and surface states of the TiO$_2$ semiconductor, probably through iridium–TiO$_2$ electronic interactions. The way of introducing iridium to the surface of TiO$_2$, *e.g.* the preparation method, is a very important factor influencing modification effects. Photodeposition appears to be a more feasible method, which accordingly leads to better photocatalytic activities.

For Ir/TiO$_2$ prepared by photodeposition, the loading of iridium shows a distinct influence on the photocatalytic activity. The activity of Ir/TiO$_2$ increases with increasing iridium loading from 0.7 to 3.5%, reaching a maximal reaction rate of 14538 µmol h^{-1} g$_{cat}$$^{-1}$, and then declines sharply with the iridium loading further increased to 6.6%. The UV-vis spectra in Fig. 4 show that the maximal light absorption in the 315–420 nm region is obtained on Ir/TiO$_2$-p at an iridium loading of 3.5%. The PL spectra in Fig. 5 reveal that the photoluminescence intensity of Ir/TiO$_2$-p, which represents the irradiative recombination of photogenerated electrons and holes, decreases with increasing iridium loading and then arrives at a minimum at an iridium loading of 3.5%. The photoluminescence intensity increases inversely with a further iridium loading increase to 6.6%. The heavy iridium loading of 6.6% results in excess iridium clusters with larger sizes on the TiO$_2$ surface, which may provide new sites for the irradiative recombination of photogenerated electrons and holes. The UV-vis and PL spectra clearly indicate that the
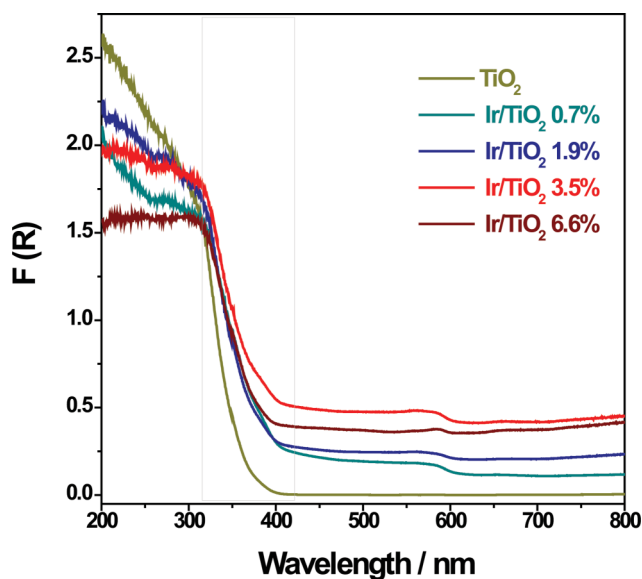
Fig. 4 Diffuse reflectance UV-vis spectra of Ir/TiO$_2$-p with different iridium loadings.
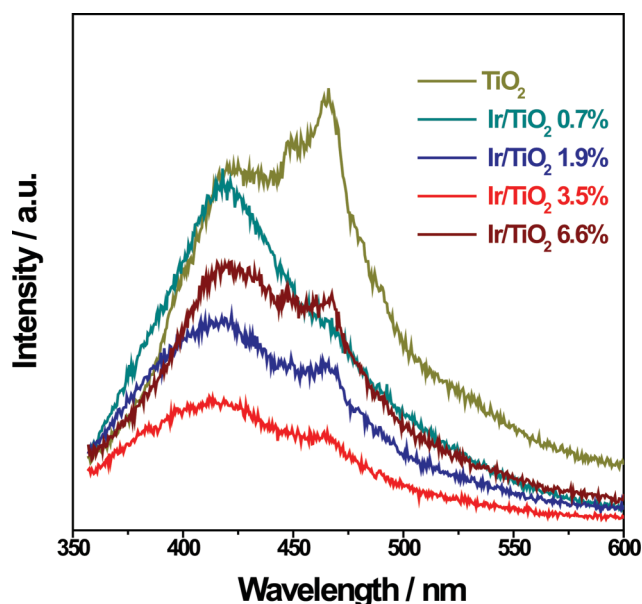

Fig. 5 PL spectra of Ir/TiO$_2$-p with different iridium loadings.

optimal iridium loading for surface modification on TiO$_2$ is *ca.* 3.5%, consistent with the photocatalytic activities.

Product selectivity in photocatalytic oxidation reactions

In past decades, photocatalytic oxidation processes have been extensively applied to the degradation of organic pollutants to carbon dioxide.[10,11] To develop photocatalytic oxidation as a green oxidation route for organic synthesis, a key point is to achieve a high selectivity towards the desired product. Meanwhile for the selective photocatalytic oxidation of alcohols in water suspensions, a rather poor selectivity to carbonyl compounds is obtained due to the generation of non-selective ˙OH radicals.[17,18] Recently, it has been reported that high selectivity can be achieved in TiO$_2$-catalyzed photocatalytic

oxidation reactions performed in benzotrifluoride or acetonitrile solvent, where the generation of ˙OH radicals and non-selective autooxidation can be avoided.[19,23] In this work, a high selectivity of over 90% to benzaldehyde can be obtained for benzyl alcohol photocatalytic oxidation over Ir/TiO$_2$-p after a time-on-stream of 6 h when the conversion is below 10%. Further extension of the reaction time leads to an obvious change in the product selectivity, as shown in Fig. 6. It is seen that the benzyl alcohol conversion gradually increases to *ca.* 45% within a time-on-stream of 40 h. The selectivity to benzaldehyde decreases with increasing benzyl alcohol conversion, while the selectivity to benzylbenzoate increases. Meanwhile, the selectivity to benzoic acid and CO$_2$ is kept at a low level of below 5% during the whole reaction process. The experimental results from the photocatalytic oxidation of pure benzaldehyde indicate that benzaldehyde can be easily oxidized to benzoic acid over Ir/TiO$_2$-p with a reaction rate of *ca.* 30687 μmol h^{-1} g$_{cat}^{-1}$ under similar reaction conditions. However, we cannot observe the accumulation of benzoic acid because the formed benzoic acid readily reacts with benzyl alcohol to produce benzylbenzoate *via* a possible photochemical process. Based on the time-dependent product selectivity during the photocatalytic oxidation of benzyl alcohol, it is easily concluded that the complete oxidation of benzyl alcohol to CO$_2$ can be efficiently suppressed under solvent-free conditions when the formation of ˙OH radicals can be avoided. Meanwhile, the oxidation of formed benzaldehyde to benzoic acid and subsequent esterification cannot be avoided, especially at high levels of benzyl alcohol conversion. The formation of acids and esters should be a common problem for the selective photocatalytic oxidation of primary alcohols. If carbonyl compounds (benzaldehyde, benzoic acid and benzylbenzoate) are calculated as the desired products, a high selectivity of >95% can be obtained, even at very high levels of benzyl alcohol
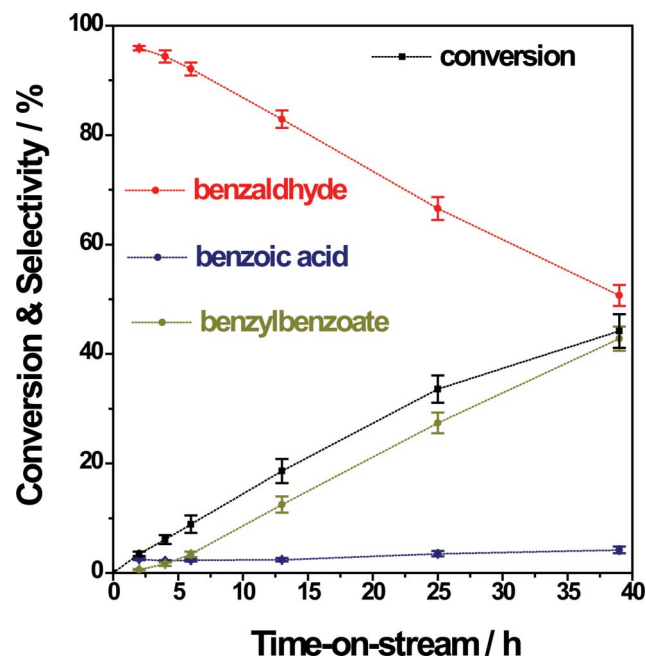

Fig. 6 Benzyl alcohol conversion and product selectivity during the selective photocatalytic oxidation of benzyl alcohol over Ir/TiO$_2$ prepared by photodeposition up to a time-on-stream of 40 h.

conversion. It should be mentioned that for the photocatalytic oxidation of secondary alcohols, a perfect selectivity to ketones can be obtained since the further oxidation of ketones can be easily avoided. For example in the experiment of α-phenylethyl alcohol photocatalytic oxidation, a reaction rate of 17289 $\mu mol\ h^{-1}\ g_{cat}^{-1}$ and >99% selectivity to acetophenone can be obtained over Ir/TiO$_2$ under reaction conditions similar to those employed for benzyl alcohol oxidation. From this point of view, the selective photocatalytic oxidation of secondary alcohols might be a more promising green oxidation reaction for applications.

Mechanism for the photocatalytic oxidation of benzyl alcohol

The changes in state of Ir/TiO$_2$-p before and after the photocatalytic oxidation of benzyl alcohol were investigated by means of XPS, and the results are shown in Fig. 7. In the Ir 4f region,
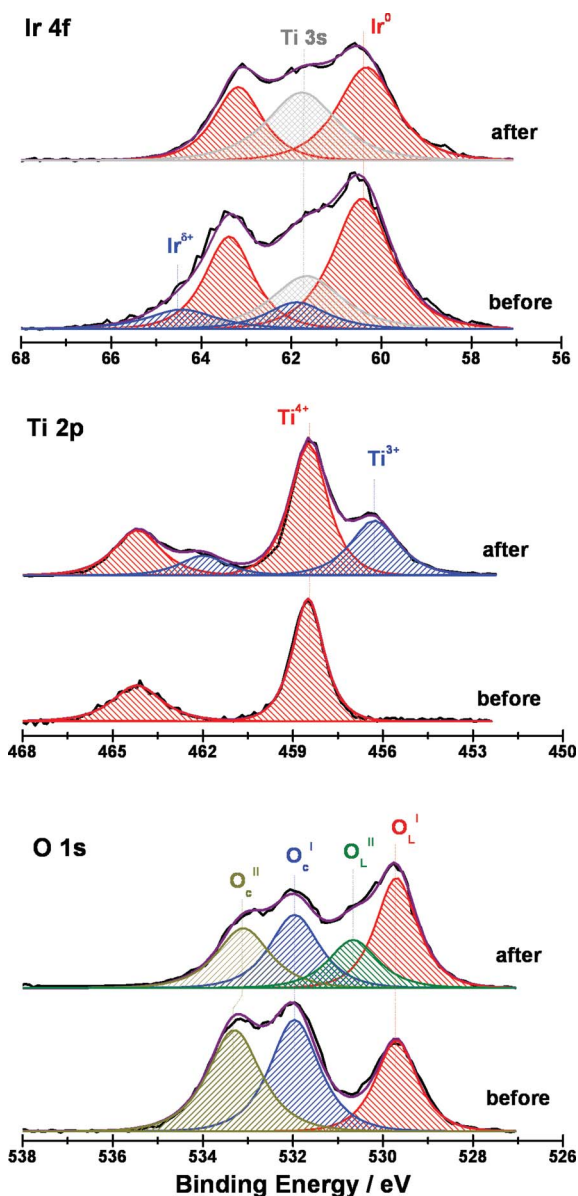

Fig. 7 X-Ray photoelectron spectra of Ir/TiO$_2$ prepared by photodeposition before and after the photocatalytic oxidation of benzyl alcohol.

binding energy values at 60.3, 61.8, 63.2 and 64.6 eV are observed for Ir/TiO$_2$ before the reaction. The binding energy values at 60.3 and 63.2 eV are assigned to 4f$_{7/2}$ and 4f$_{5/2}$ of metallic iridium, while those at 62.0 and 65.0 eV are assigned to 4f$_{7/2}$ and 4f$_{5/2}$ of iridium oxides.[34] It is clear seen that both metallic iridium and iridium oxides exist in Ir/TiO$_2$ prepared by photodeposition. After the photocatalytic reaction, the binding energy values assignable to iridium oxides disappear, indicating the reduction of iridium oxides to metallic iridium.

Further experiments reveal that iridium oxides cannot be reduced by benzyl alcohol without irradiation, and therefore iridium oxides should be reduced by photogenerated electrons during the irradiation.

In the Ti 2p region, binding energy values at 458.5 and 464.2 eV, assignable to 2p$_{3/2}$ and 2p$_{1/2}$ of Ti^{4+} in TiO$_2$, are observed before the reaction. The appearance of binding energy values at 456.2 and 461.8 eV, assignable to Ti^{3+},[35] indicates the partial reduction of Ti^{4+} to Ti^{3+} during the photocatalytic reaction. In the O 1 s region, binding energy values at 529.8, 531.9 and 533.3 eV are observed in Ir/TiO$_2$-p before the reaction. The binding energy value at 529.8 eV (O$_L^I$) is assigned to crystal lattice oxygen in O-Ti^{4+}, while the binding energy values at 531.9 (O$_C^I$) and 533.3 eV (O$_C^{II}$) are assigned to chemisorbed oxygen in hydroxyl-like groups.[36,37] After the photocatalytic reaction, a new binding energy value at 530.7 eV (O$_L^{II}$), assignable to lattice oxygen in O-Ti^{3+},[38] appears, which confirms the reduction of Ti^{3+} in Ir/TiO$_2$ after the reaction. Meanwhile, the binding energy value assignable to chemisorbed oxygen (O$_C^{II}$) changes slightly from 533.3 to 533.0 eV, probably related to the change in the existence states of iridium.

A primary reaction scheme for the selective photocatalytic oxidation of benzyl alcohol over Ir/TiO$_2$ is proposed, as shown in Fig. 8. Under ultraviolet irradiation, electron–hole pairs are created on the semiconductor Ir/TiO$_2$. Since the work function of iridium is higher than that of TiO$_2$, the photogenerated electrons tend to migrate from TiO$_2$ to the iridium clusters, whereas the photogenerated holes are left in the TiO$_2$. The photogenerated electrons are trapped in the iridium clusters and result in the reduction of iridium oxides to metallic iridium species, as proved by the XPS results. During the photocatalytic reaction, the benzyl alcohol molecules are adsorbed onto the surface of the TiO$_2$ and react with the photogenerated holes to produce carbon radicals, accompanied by the reduction of Ti^{IV} in TiO$_2$ to Ti^{III} through electron transfer. Molecular
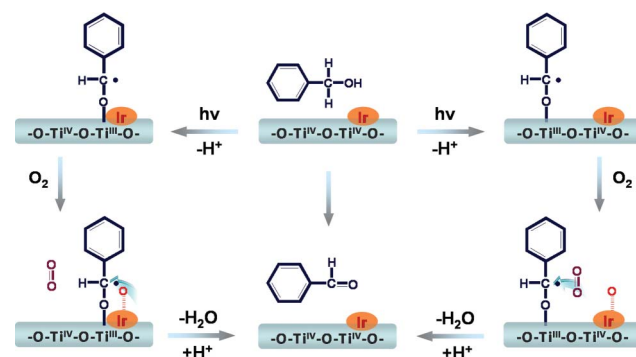

Fig. 8 Mechanism for the selective photocatalytic oxidation of benzyl alcohol over Ir/TiO$_2$.

oxygen prefers to be adsorbed onto the iridium clusters and easily dissociates to chemisorbed oxygen atoms due to the low dissociation barrier.[39] The chemisorbed oxygen atoms can diffuse to the adjacent TiO_2 surface, where they react with carbon radicals to produce benzaldehyde as well as oxidize Ti^{III} to Ti^{IV}. Meanwhile, for the carbon radicals and the Ti^{III} located far away from the iridium clusters, they can only be oxidized by molecular oxygen. Because the oxidative reactivity of molecular oxygen is much weaker than that of chemisorbed oxygen atoms, the reaction between carbon radicals and chemisorbed oxygen atoms make a major contribution to the total photocatalytic oxidation activity. Since molecular oxygen prefers to be adsorbed onto the iridium clusters, the anaerobic photocatalytic oxidation of benzyl alcohol on TiO_2 may also proceed *via* a two-electron transfer process, as suggested by Zhang *et al.*[23] In the whole photocatalytic process, part of the Ti^{III} species cannot be re-oxidized to Ti^{IV}, and therefore can be detected by means of XPS.

Based on the characterization and catalytic results, the modification effects of iridium on TiO_2 are ascribed to the following two aspects. On the one hand, the deposition of iridium clusters on the surface of TiO_2 efficiently suppresses the recombination of photogenerated holes and electrons in the TiO_2 semiconductor, which is certainly good for various photocatalytic processes. On the other hand, the introduction of iridium clusters onto TiO_2 especially favors the activation of molecular oxygen and therefore promotes the participation of molecular oxygen in selective photocatalytic oxidation reactions.

Photocatalytic oxidation of benzyl alcohol over Pd-Ir/TiO₂

Ir/TiO_2 prepared by photodeposition shows a promising activity for the photocatalytic oxidation of benzyl alcohol, and we have therefore tried to improve the photocatalytic activity of Ir/TiO_2-p by introducing a second metal. After comprehensive screening, we found that only palladium appears to be an effective second modifier of Ir/TiO_2, and $Pd-Ir/TiO_2$ prepared by co-instantaneous photodeposition showed a distinctively improved activity for the photocatalytic reaction. It was found that the Pd/Ir ratio greatly influenced the photocatalytic activity of $Pd-Ir/TiO_2$-p. As seen in Table 3, the optimal Pd : Ir ratio was 1 : 1, where a very high reaction rate of 41713 μmol h⁻¹ g_{cat}^{-1} (*ca.* three-times higher than Ir/TiO_2-p) with an 82% selectivity to benzaldehyde could be obtained. Meanwhile, Pd-

Ir/TiO_2 prepared by co-instantaneous wet impregnation and chemical reduction also showed higher activities than Ir/TiO_2 prepared by the same methods (Table 2 and Table 3). That is to say, palladium is a universal effective modifier to Ir/TiO_2, no matter which preparation method is employed. UV-vis and PL spectra results (not shown here) revealed that the addition of palladium did not change the light absorption, and recombination of photogenerated electrons and holes under irradiation. Therefore, the modification effects of palladium on Ir/TiO_2 are hypothesized to be related with the promotion of oxygen activation and the enhancement of oxygen mobility during the photocatalytic reaction. Further research on this topic is in progress.

Conclusions

The solvent-free selective photocatalytic oxidation of benzyl alcohol in the presence of molecular oxygen can be achieved using TiO_2 and transition metal-modified TiO_2 as photocatalysts under ultraviolet irradiation. The surface modification of TiO_2 by transition metal clusters can dramatically enhance its photocatalytic performance. The type of transition metal, preparation method, metal loading and reaction conditions all show obvious impacts on the photocatalytic oxidation of benzyl alcohol. Typically, a high benzyl alcohol photocatalytic oxidation activity as well as a high selectivity to carbonyl compounds can be obtained on Ir/TiO_2 prepared by photodeposition. The deposition of iridium clusters on the surface of TiO_2 can suppress the recombination of photogenerated holes and electrons in the TiO_2 semiconductor, which is good for photocatalytic reactions. Moreover, the existence of iridium clusters on TiO_2 especially favors the activation of molecular oxygen and greatly promotes the participation of molecular oxygen in selective photocatalytic oxidation reactions.

In the photocatalytic oxidation of benzyl alcohol, the reaction between carbon radicals and chemisorbed oxygen atoms make a major contribution to the total photocatalytic oxidation activity, while the reaction between carbon radicals and molecular oxygen, as well as the anaerobic photocatalytic oxidation of benzyl alcohol, on TiO_2 may also proceed.

Under solvent-free conditions, the formation of ˙OH radicals is suppressed, and therefore the complete oxidation of benzyl

Table 3 Selective photocatalytic oxidation of benzyl alcohol over Pd-Ir/TiO₂[a]

Catalyst	Metal loading[b] (%)	Pd : Ir[c]	Metal size[d]/nm	Conversion (%)	Product Selectivity (%)			Reaction rate[g] / μmol h⁻¹ g_{cat}^{-1}
					Benzaldehyde	Carbonyls[e]	Others[f]	
Pd-Ir/TiO₂-i	Pd: 1.9; Ir: 1.8	1 : 1	4.1	5.2	87	98	2	8403
Pd-Ir/TiO₂-c	Pd: 1.8; Ir: 1.8	1 : 1	3.9	4.5	86	97	3	7288
Pd-Ir/TiO₂-p	Pd: 1.8; Ir: 1.7	1 : 1	3.1	25.6	82	94	6	41713
Pd-Ir/TiO₂-p	Pd: 3.2; Ir: 0.6	5 : 1	2.7	12.0	77	96	4	19538
Pd-Ir/TiO₂-p	Pd: 2.6; Ir: 1.2	4 : 2	2.9	19.5	88	96	4	31789
Pd-Ir/TiO₂-p	Pd: 1.2; Ir: 2.4	2 : 4	3.1	18.1	84	95	5	29463
Pd-Ir/TiO₂-p	Pd: 0.6; Ir: 3.1	1 : 5	3.2	11.3	86	97	3	18425

[a] Reaction conditions: catalyst 0.3 g, benzyl alcohol 0.3 mol, reaction *T* 333 K, reaction time 6 h. [b] Analyzed by ICP. [c] Designed ratio. [d] Average size observed by TEM. [e] Including benzaldehyde, benzoic acid and benzylbenzoate. [f] Including CO_2 and other unknown products. [g] Rate of benzyl alcohol oxidation per unit of catalyst per unit time.

alcohol to CO_2 can be largely avoided. However, the further oxidation of formed benzaldehyde to benzoic acid and subsequent esterification cannot be avoided, especially at high levels of benzyl alcohol conversion. This is probably a common problem for the selective photocatalytic oxidation of primary alcohols. In contrast, perfect selectivity to ketones can be achieved in the photocatalytic oxidation of secondary alcohols since the further oxidation of ketones can be easily avoided.

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