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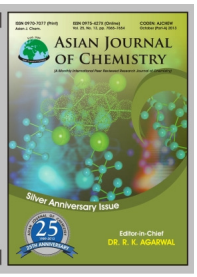

Visible Light Responsive Photocatalytic Degradation of 4-Chlorophenol on Neat TiO_2 by Surface-Complex-Mediated Path

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The visible light responsive photocatalytic degradation of 4-chlorophenol was investigated in aqueous suspension of pure TiO_2 under visible light by a surface-complex-mediated path. The addition of *tert*-butyl alcohol, a common OH radical scavenger, did not affect the visible activity of 4-chlorophenol, which indicates that OH radicals are not responsible for the degradation. UV-Visible result indicated that the surface complexation between phenolic compounds and TiO_2 was formed, which was responsible for the visible light activity. The activity decreased dramatically after Pt deposition. The photocatalytic activity increased with increasing the S_{BET} of the catalyst. The crystal proportion of catalyst strongly influence the photocatalytic activity. The possible mechanism was investigated.

Key Words: TiO_2, 4-Chlorophenol, Photocatalytic degradation, Visible light.

INTRODUCTION

Titanium dioxide has been intensively investigated as a photocatalyst and is still the most efficient, most practical and most studied photocatalyst despite extensive efforts to find photocatalytic materials outperforming TiO_2. TiO_2 photocatalysts can destruct almost all organic pollutants on UV irradiated TiO_2 surface[1,2]. However, the lack of visible light activity has been a major obstacle to limit the practical application of TiO_2 photocatalyst. There have been many attempts to make TiO_2 or other wide band-gap semiconductors photoactive under visible light illumination[3-8]. Photosensitization is one of the most widely used methods to extend the photoresponse of TiO_2 into the visible region. Cho *et al.*[9], recently reported that pure TiO_2 in aqueous solution of a nonionic surfactant having polyoxyethylene groups (Brij) exhibited visible light activity for the reduction of CCl_4 and Cr(VI) and observed a broad absorption band (320-500 nm) in the Brij/TiO_2 solution. They proposed that a complex formation between the surfactant functional group and TiO_2 surface is responsible for the weak visible light absorption and the subsequent visible-light-induced electron transfer. Agrios *et al.*[10,11] also observed that 2,4,5-trichlorophenol formed a charge-transfer complex on TiO_2 and correlated the charge transfer surface complex formation with visible light absorption among several chlorophenols. The visible-light-induced transformation of 2,4,5-trichlorophenol on TiO_2 produced coupling products only and no mineralization was achieved. They reported that the charge-transfer complex formation was highly favoured with P25 TiO_2 that has mixed phases of anatase and rutile and that the complexation on pure-phase anatase or rutile was significantly reduced. The above examples share a similarity in that surface complex formation on pure TiO_2 is responsible for the visible-light-induced photocatalytic transformation of substrates that do not absorb visible photons by themselves.

Since a majority of TiO_2 photocatalytic reactions have been studied under UV irradiation, the potential visible light reactivities of TiO_2 due to the surface complex formation mechanism seem to be largely unrecognized. There should be more examples of such surface complexation that has visible light activity. In this study, we demonstrated that 4-chlorophenol, which is one of the most common substrates that have been used in the studies of photocatalytic degradation, can be actually degraded and mineralized under visible irradiation. The visible light reactivity of 4-chlorophenol was correlated with the surface complex formation that was supported by the diffuse reflectance UV-visible spectra. Various experimental evidence for the visible light reactivity of 4-chlorophenol was presented and discussed. The possible mechanism was investigated.

EXPERIMENTAL

Surface platinized P25 (Pt-P25) was obtained using a photodeposition method as described elsewhere[12,13], 0.5 g L^{-1} of P25 suspension with 1 M methanol (electron donor) and 0.1 mM chloroplatinic acid (H_2PtCl_6) was irradiated with a 200 W mercury lamp for 0.5 h. After irradiation, Pt-deposited

P25 powder was filtered, washed with distilled water and dried under air. A typical Pt loading on P25 was estimated to be 3 wt %.

Suspensions were prepared in deionized water by mixing TiO_2 catalyst with appropriate solutions of trichlorophenol. In a typical procedure, 0.1 g TiO_2 powders were dispersed in 100 mL solution of trichlorophenol (initial concentration $C_0 = 60 \times 10^{-6}$ g mL^{-1}) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor and stirred for 0.5 h in darkness to achieve the adsorption equilibrium. In the photoreaction under visible light irradiation, the suspension was exposed to a 110-W high-pressure sodium lamp with main emission in the range of 400-800 nm and air was bubbled at 130 mL/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M $NaNO_2$ solution. In the investigation of photodegradation by UV light, a 125 W high-pressure mercury lamp with a water cooling cylindrical jacket was used. All runs were conducted at ambient pressure and 30 ºC. The conversion of trichlorophenol was determined using an Agilent 1100 series HPLC operated in isocratic mode under the following conditions: methanol-water (80:20 %); flow rate 1 mL min^{-1}; temperature 25 ºC; Column Phenomenex Luna 10 µ phenyl-hexyl, 4.6 mm × 250 mm; detector UV at 254 nm; injection volume 5 µL. For comparison, methylene blue was used as substrate following the same procedure above.

UV-VIS spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using $BaSO_4$ as the reference sample. An organic substrate such as 4-chlorophenol was added to aqueous TiO_2 suspension in the same concentration ratio as in the case of photocatalytic reaction. The Brunauer-Emmett-Teller (BET)-specific surface areas (S_{BET}) of the samples were determined through nitrogen adsorption at 77K (Micromeritics ASAP 2010). All the samples were degassed at 393 K before the measurement.

RESULTS AND DISCUSSION

Fig. 1 shows the photocatalytic performances of P25 in the degradation trichlorophenol and methylene blue under UV and visible light irradiation. In the previous report, Lettmann *et al.*[14] reported that 6 and 15 % of 4-chlorophenol was degraded after 100 min under visible light irradiation ($\lambda > 400$ nm) with Degussa P25. They ascribed this visible light activity to traces of UV light leaking into a reactor. In this investigation, the conversion of methylene blue was 100 % under UV light within 4 h, whereas almost no activity was observed in the degradatiob of methylene blue under visible light. This indicated that no UV light was leaked into the reactor. However, it is shown in Fig. 1 that the conversion of 4-chlorophenol was more than 85 % under visible light. This indicated that 4-chlorophenol can be degraded on pure TiO_2 under visible light. Besides, compare two conversions under visible light (methylene blue and 4-chlorophenol), it indicated that some especial surface complex which is responsible for the vis-activity may informed between P25 and 4-chlorophenol.

It is known that both pure TiO_2 and 4-chlorophenol do not absorb the visible light. Fig. 2 shows the UV-visible spactra of P25 before and after 4-chlorophenol adsorption. Obviously,

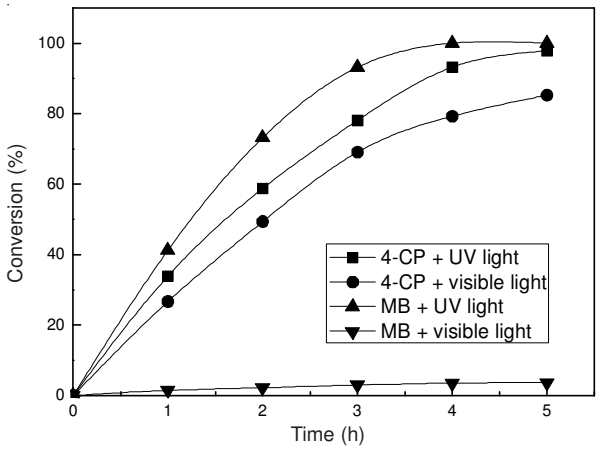


Fig. 1. Photocatalytic performances of P25 in the degradation trichlorophenol and methylene blue under UV and visible light irradiation

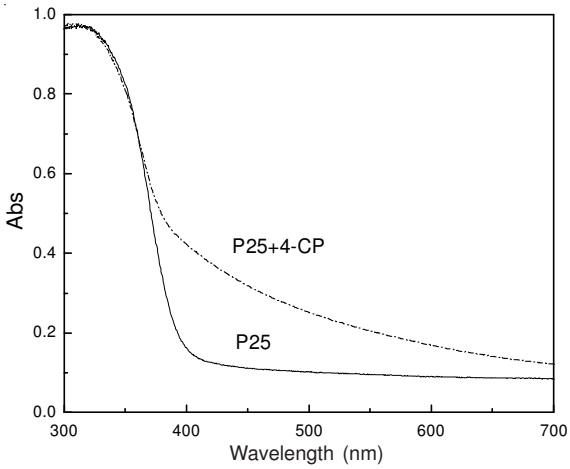


Fig. 2. UV-visible spactra of P25 before and after 4-chlorophenol adsorption

pure P25 did not absorb visible light. However, it is noted that, the absorption of P25 in the visible light was obvious improved after 4-chlorophenol adsorption. The visible light absorption by the TiO_2/phenolic compound powders indicates that surface complexes form between TiO_2 and phenolic compounds. The most probable structure is that the substrate is attached to the surface through a phenolate linkage, as following reaction:

$$\equiv Ti{-}OH + OH{-}Ph \rightarrow \equiv Ti{-}O{-}Ph + H_2O$$

This kind of surface complexation enables the visible light absorption through ligand-to-metal charge transfer (LMCT) between the substrate (ligand) and the Ti(IV) site on the surface[15,16]. Such LMCT mechanism has been reported by many groups. Seo *et al.*[17] demonstrated that the LMCT mediated visible light absorption is enabled not only by the covalent bonding (inner-sphere complexation) like reaction above but also by the physical adsorption (outer-sphere complexation) of polyaromatic hydrocarbons on TiO_2. Stafford *et al.*[18] also reported that 4-chlorophenol adsorbed on dry TiO_2 powder changed the colour of TiO_2 from white to yellow and suggested the phenolate linkage formation on the basis of the measurement of diffuse reflectance FTIR spectroscopy.

Effects of *tert*-butyl alcohol (TBA, 10 mM) addition and Pt deposition on the photocatalytic performances of P25 under

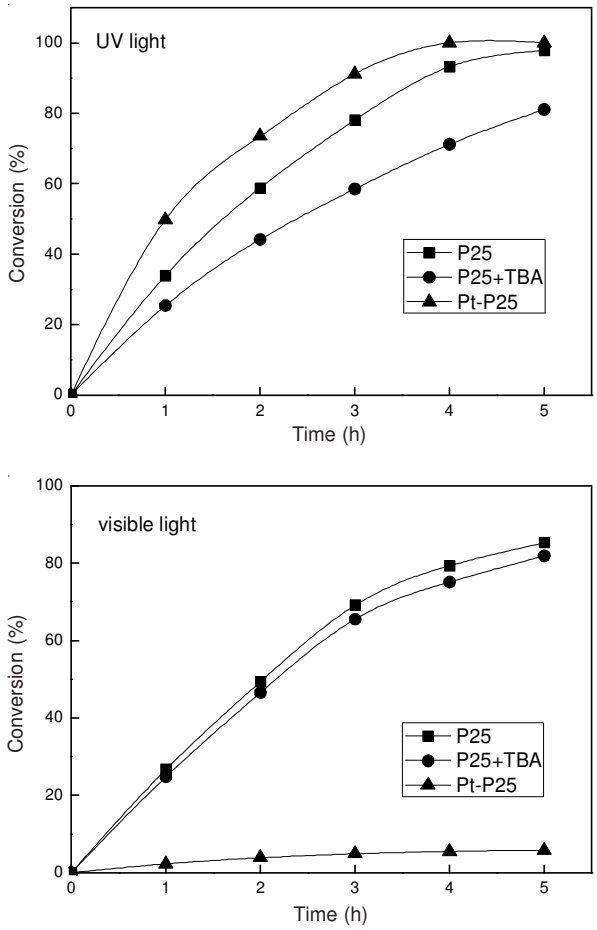


Fig. 3. Effects of tert-butyl alcohol (TBA, 10 mM) addition and Pt deposition on the photocatalytic performances of P25 under UV and visible light

UV and visible light are shown in Fig. 3. When *tert*-butyl alcohol was added as an OH radical scavenger, the activity of P25 was decreased obviously under UV light. However, it little affected the degradation of 4-chlorophenol under visible irradiation. Since OH radicals can not be generated on visible-light-illuminated TiO_2, the VIS-activity should not be mediated by OH radicals. Besides, surface platinization of TiO_2 highly enhanced the degradation of 4-chlorophenol under UV irradiation but strongly inhibited the degradation of 4-chlorophenol under visible light. In general, Pt deposits on TiO_2 trap photogenerated conduction band electrons, subsequently retards the charge pair recombination and enhances the overall degradation rates[19,20]. Surface fluorination of TiO_2 increases the mobile OH radical generation and enhances the OH radical mediated degradation rate[21,22]. The fact that the visible-light-induced degradation of 4-chlorophenol was almost completely inhibited when the TiO_2 surface was modified implies that the surface interaction of 4-chlorophenol on TiO_2 plays a critical role somehow in the vis-activity mechanism. When P25 was modified by Pt, such surface interaction was broken, leading to the poor activity.

It has been proved that the vis-activity was attributed to the surface complex. Therefore, S_{BET} should be a important factor which influence the activity. In this investigation, pure anatase TiO_2 with different S_{BET} was prepared (preparation method will be published elsewhere). Fig. 4 shows the

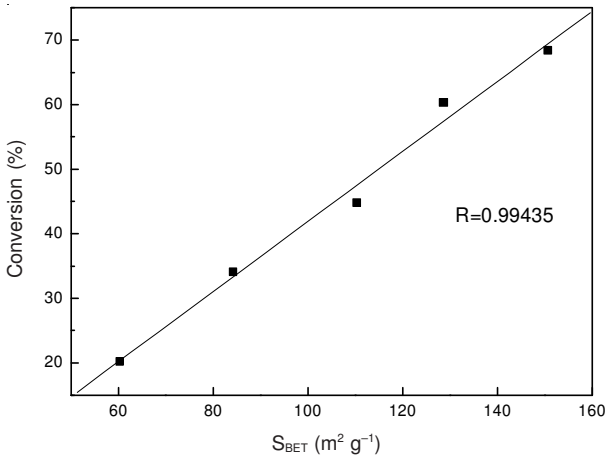
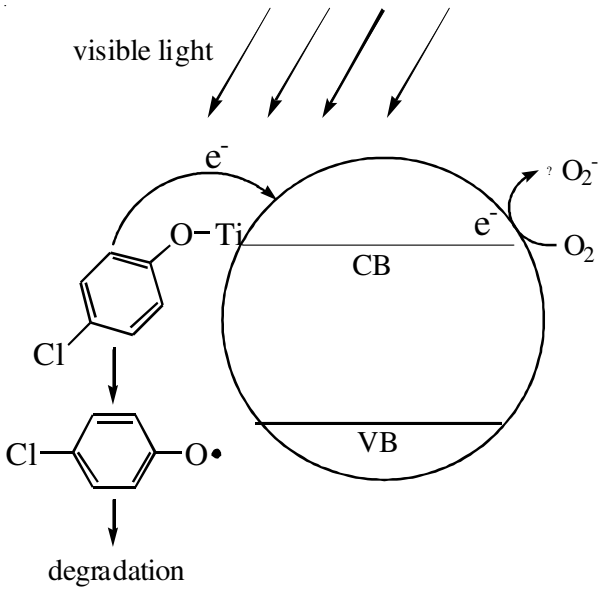


Fig. 4. Relationship between S_{BET} of catalyst and trichlorophenol conversion

relationship between S_{BET} of catalyst and trichlorophenol conversion. The good linear relationship was shown (R = 0.99435), which proved the importance of S_{BET} on the activity. However, it is noted that the activity of pure anatase TiO_2 was much lower than that of P25, although it exhibited bigger SBET. Agrios *et al.*[11] claimed that P25 is better than pure anatase TiO_2 in surface complexation and visible activity of chlorophenols because of the mixed crystallinity of the former.

In summary, the mechanism is now quite clear. **Scheme-I** exhibited surface-complex-mediated photodegradation of 4-chlorophenol on pure TiO_2 under visible irradiation. The TiO_2/4-chlorophenol surface complex is excited by visible light through LMCT with direct transfer of an electron from 4-chlorophenol to TiO_2 conduction band, which is subsequently followed by a series of degradation reactions of 4-chlorophenol. The visible light induced electron transfer from 4-chlorophenol to conduction band in **Scheme-I** is a direct transition without involving the excited state of 4-chlorophenol. Once an electron is injected into conduction band, it should be transferred to suitable electron acceptors. Otherwise it recombines with the surface complex to make a null cycle.



Scheme-I: Surface-complex-mediated photodegradation of 4-chlorophenol on pure TiO_2 under visible irradiation

Conclusion

The visible light responsive photocatalytic degradation of 4-chlorophenol was investigated in aqueous suspension of pure TiO_2 under visible light by a surface-complex-mediated path. This kind of surface complexation enables the visible light absorption through ligand-to-metal charge transfer (LMCT) between the substrate (ligand) and the Ti(IV) site on the surface. The addition of *tert*-butyl alcohol, a common OH radical scavenger, did not affect the visible activity of 4-chlorophenol, which indicates that OH radicals are not responsible for the degradation. UV-visible result indicated that the surface complexation between phenolic compounds and TiO_2 was formed, which was responsible for the visible light activity. The good linear relationship was observed between S_{BET} of catalysts and the photocatalytic activity. P25 with mixed crystallinity showed much higher activity than that of pure anatase TiO_2.

ACKNOWLEDGEMENTS

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