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Synthesis and characterization of TiO_2 chemically modified by Pd(II) 2-aminothiazole complex for the photocatalytic degradation of phenol

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Abstract

An investigation was made into the photocatalytic activity of *in situ* synthesized TiO_2 chemically modified by Pd(II) 2-aminothiazole complex for phenol degradation at different pH values. At longer reaction times, the bare titania presented far poorer photoactivity than the modified catalysts in the entire range of pH studied. The catalyst complexed with Pd(II) was more efficient than the metal-free Pd, irrespective of pH and reaction time, suggesting that metal plays an important role. A cooperative mechanism is proposed, involving the possible photoactivation of both TiO_2 and sensitizer.

Keywords: Pd(II) 2-aminothiazole; TiO_2; Phenol photodegradation; Photosensitization

1. Introduction

Heterogeneous photocatalysis using semiconductors has been commonly employed as a convenient tool for environmental remediation due to its high power of degradation of a large variety of organic pollutants [1–5]. Among the various semiconducting metal oxides, titanium dioxide (TiO_2) is probably the most widely studied and applied photocatalyst for its low commercial cost, nontoxicity, photostability, chemical stability over a wide pH range, etc. [6,7]. However, fundamental problems concerning the efficiency of this photocatalyst still need to be solved. Firstly, its large band-gap (3.2 eV), which limits the use of sunlight as an energy source for degradation of organic contaminants since a significant part of the solar energy reaching the earth's surface lies in the visible and near infrared region of the spectrum ($\lambda > 400$ nm). Secondly, rapid hole–electron recombination, which causes photocatalytic processes to produce a low quantum yield.

Photosensitization via surface adsorbed organic dyes and coordination metal complexes, one of several approaches to sensitize photocatalytic properties of TiO_2 towards visible radiations, has received special attention [8–11]. Among numerous modes of anchoring surface chemical modifying agents onto TiO_2, covalent attachment is probably the most widely adopted approach [12]. Carboxyl, phosphonate, amino and silyl functionalities have been shown to form linkages with the TiO_2 surface. However, all conventional covalent linkages, with the exception of the silyl anchoring group, undergo a certain degree of dissociation or dechelation. The silyl anchoring group seems to be an ideal surface modification moiety for TiO_2 owing to the strong interaction of the silyl functionality with the hydroxyl groups on the surface of the semiconductor and the chemical inertness of the resulting Ti–O–Si–C bonds [13]. Photosensitized TiO_2 using silylated tris(3-(pyridin-2-yl)pyrazole)ruthenium(II) was able to mediate the photodegradation of perhalogenated organics in aqueous medium under diffused visible irradiation [14].

In this paper, we report on the *in situ* synthesis and photochemical properties of a new photocatalyst, TiATPd, where AT is the ligand 2-aminothiazole attached to surface oxide modified by organoalkoxysilane 3-chloropropylmethoxysilane.

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The AT presents double conjugated insaturations, two heteroatoms and an amino group that allows for the coordination of metal ions such as palladium(II), leading to the formation of the above complex. We also evaluate the photocatalytic activity of this complex towards phenol degradation under UV irradiation.

2. Experimental

2.1. Chemicals

The chemicals 2-aminothiazole (Aldrich), 3-chloropropylmethoxysilane (Merck), $Pd(NO_3)_2$ (Merck) and phenol (Merck), of reagent grade, were used without further purification. The *N*,*N*-dimethylformamide (DMF) utilized was ACS reagent grade (J.T. Baker), and was stored for 48 h on activated molecular sieves (4 Å) before use. Titania, supplied by Degussa (P25), was predried at 150 °C under vacuum for 10 h and then used immediately.

2.2. Organofunctionalization

Fifty grams of preactivated titania (0.02 mol of active sites) [8,15] was suspended in 200 mL of dried DMF containing 7.34 mL of 3-chloropropylmethoxysilane (SiCl). The mixture was refluxed by magnetic stirring in an N_2 atmosphere for 72 h at approximately 150 °C. The resulting product (TiPCl) was collected by filtration, washed with DMF, ethanol and distilled water and vacuum-dried at 100 °C for 8 h.

2.3. Immobilization of AT on organofunctionalized titania

Forty-five grams of predried organofunctionalized titania, TiPCl, was added to 200 mL of dried DMF and 4 g of AT. The sample was kept under agitation, reflux and N_2 atmosphere for 48 h at ∼150 °C. The functionalized titania with AT (TiAT) was collected by filtration, washed repeatedly with DMF, ethanol and finally with distilled water and vacuum-dried at 100 °C for 8 h.

2.4. Coordination of Pd(II) by TiAT

A mixture containing 3 g of the functionalized titania with AT, TiAT, and 200 mL of aqueous solution of $Pd(NO_3)_2$ ($1\ g\ L^{-1}$) was kept under magnetic stirring away from light for 3 h. The resulting product, TiATPd, was filtered off, washed repeatedly with distilled water and vacuum-dried for 48 h at room temperature.

2.5. Characterization

The quantity of AT anchored on titania was determined by nitrogen analysis using the Kjeldhal method [16]. Diffuse reflectance infrared Fourier transform (DRIFTS) spectroscopy was carried out on a Nicolet Nexus 670 spectrometer. One hundred scans were accumulated for each spectrum at a spectral resolution of $8\ cm^{-1}$ and slit opening of 100 nm. Absorption spectra in the UV–vis range were recorded using a Thermo-Spectronic model Genesys 6 spectrophotometer. The organic carbon content was analyzed using a Shimadzu Instruments, model TOC-V_{CPH} total organic carbon analyzer. The specific surface area was determined by the BET method [17] using an automated Micromeritics ASAP 2010 analyzer. Prior to taking the measurements, the samples were vacuum-dried at 70 °C for 72 h. Solid-state ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Mercury Plus 300 spectrometer at room temperature in a 7 mm silicon nitrite rotor, operating at 75.47 and 59.61 MHz for carbon and silicon, respectively, using a combination of the cross-polarization and magic angle spinning (CP/MAS) methods. The magic-angle spinning speed was 3 kHz, the time repetition was 2 s for both nuclei, and the contact time was 2 ms for silicon and 4 ms for carbon. The coordinated quantity of Pd was determined by inductively coupled plasma-optical emission (ICP-OES) spectrometry, using a Varian (VISTA AX CCD-Simultaneous) spectrometer with axial configuration and a V-groove nebulizer. After the photodegradation process, the Pd in solution was determined using a Shimadzu (AA-6800) atomic absorption spectrometer with graphite furnace and background correction based on the Zeeman effect.

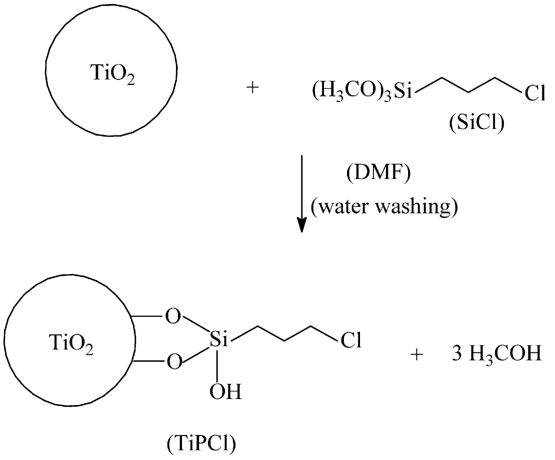
2.6. Photocatalytic experiments

The photodegradation studies were carried out with bare titania (Degussa P25), TiAT and TiATPd catalysts. All these experiments involved the use of a suspension containing 125 mg of photocatalyzer in 250 mL of a standard phenol solution ($15\ mg\ L^{-1}$). During the experiments, which were conducted in a cylindrical reactor ($264\ cm^2$), the suspensions were stirred continuously and saturated with oxygen at a temperature of 30 °C. The irradiance of $5.11\ mW\ cm^{-2}$ at $\lambda = 365$ nm, produced by four 15 W black light lamps, was measured using a Solar Light Co. Inc. model PMA2100 version 1.16 photometer/radiometer. At varied time intervals, aliquots of 5 mL were removed from the reaction mixture, filtered through 0.22 μm membranes (Millipore) and analyzed. The phenol concentrations in solutions with different pH values, controlled by employing HNO_3 and NaOH for acid and alkaline media, respectively, were determined by measuring the absorbance at $\lambda = 270$ nm, utilizing a linear calibration curve in which the phenol concentrations ranged from 1 to $15\ mg\ L^{-1}$. The concentrations were also monitored by their organic carbon content, using a linear calibration curve whose phenol concentration varied within a range of 2–15 $mg\ L^{-1}$.

3. Results and discussion

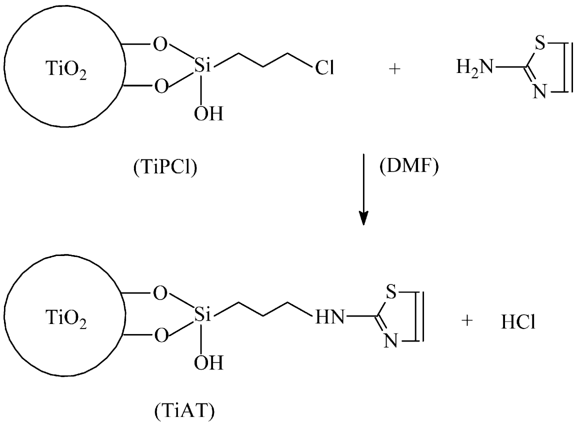
3.1. Synthesis and characterization of the photocatalysts

The synthesis of the TiATPd complex consisted basically of three steps. The first involved the modification of titania with 3-chloropropyltrimethoxysilane (SiCl), resulting in TiPCl, as shown in Eq. (1). The formation of silanol and the absence of methoxy groups were probably the result of methoxy hydrolysis by washing with water.



(1)

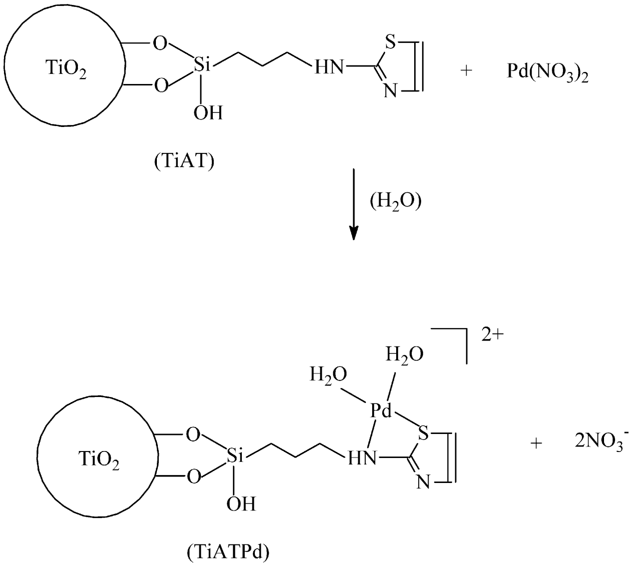
This precursor TiPCl reacted with 2-aminothiazole to form the product TiAT, as described in Eq. (2) (second step).



(2)

The nitrogen analysis of TiAT yielded (0.425 ± 0.008) mmol g^{-1} of the functional groups attached to the TiO_2 surface.

The third step consisted of the coordination of Pd(II) by TiAT, according to Eq. (3).



(3)

This reaction is based on Pearson's theory [18]; sulfur is a soft base and thus it tends to bond with soft acid such as Pd(II). The d^8 electronic configuration of Pd(II) probably produces a complex with 16 electrons and a square planar geometry [19].

The coordinated amount of Pd on TiATPd complex, determined by using ICP-OES spectrometry, yielded (0.52 ± 0.04) mmol g^{-1}.

In order to substantiate the formation of these new catalysts, they were characterized by several techniques.

The specific surface area of bare titania was (50 ± 2) $m^2\ g^{-1}$, which is consistent with the published values [20,21]. The catalyst TiAT presented a specific surface area of (36 ± 2) $m^2\ g^{-1}$. This significant decrease evidenced the chemical modification on the titania surface, which probably resulted from a steric impediment caused by anchored AT groups and recovery of the surface, making the pores less accessible to N_2 during measurements of the specific surface area. The higher the recovery of the sorbent the higher the decrease in the specific surface area. The DRIFTS spectra shown in Fig. 1 confirm the attachment of the organic and inorganic groups of interest on the titania surface. The weak absorption band at 3688 cm^{-1} in TiO_2 was assigned to the O–H stretching vibrations of hydroxyl groups [22]. The absence of this band in the modified catalysts indicates that the hydroxyl groups were completely modified by the SiCl via surface modification. Spectra of all the modified materials showed symmetrical stretching ($\nu_s CH_2$) and asymmetrical stretching ($\nu_{as} CH_2$) at 2935 and 2961 cm^{-1}, respectively, attributed to the methylene groups of the silylant, confirming the successful anchorage of silylant agent on the TiO_2 surface. The other characteristic bands of SiCl appearing at 1386, 1338 and 1471 cm^{-1} can be attributed to the bending vibrations (δCH_2) of the propyl group [23]. The broad absorption band observed in the 3000–3500 cm^{-1} region is typical of the O–H stretching frequency of hydrogen bonds assigned to Ti–OH, as well as of adsorbed water on the titania surface. The absorption band near 1630 cm^{-1}, due to O–H bending vibrations of hydroxyl groups,

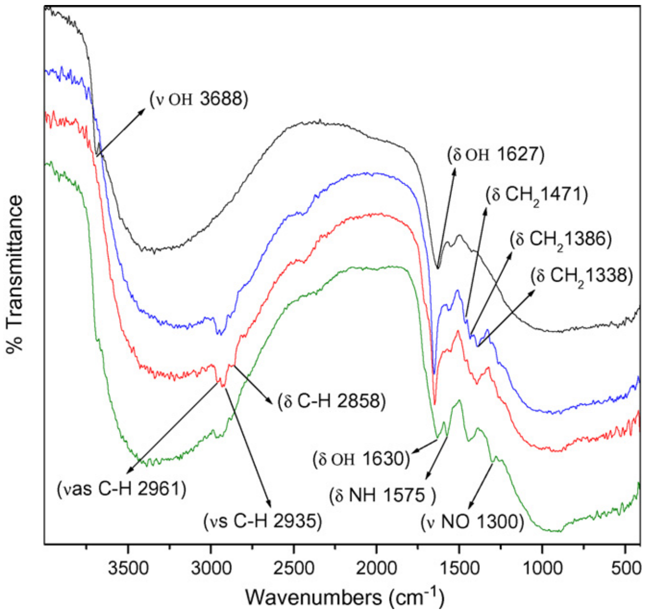


Fig. 1. DRIFTS spectra of TiO_2 (—), TIPCl (🟦), TiAT (🟧), TiATPd (🟩).

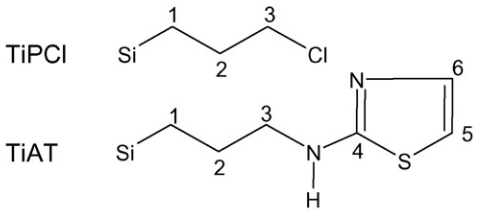


Fig. 2. Numbering used in the assignment of the carbons present in TiPCl and TiAT.

along with the absorption of silylant, made it difficult to analyze the characteristic functional groups of the AT. However, the weak absorption band at 2858 cm^{-1} may be attributed to olefinic C–H stretching [24]. The spectrum of titania functionalized with AT and coordinate Pd (TiPdAT) presents a band at 1575 cm^{-1} that may be assigned to the bending vibrations (δNH) of the –CNH– moiety of the heterocycle [23]. This datum suggests that the Pd(II) ion is coordinated to the free nitrogen of the AT and not only physically sorbed onto the surface. The existence of the band at 1300 cm^{-1} arising from the N–O stretching vibration corroborates the presence of NO_3^- counter ions in the Pd complex [25].

Solid-state ^{13}C and ^{29}Si NMR spectra confirmed the attachment of the organic molecules of interest to the titania. Figs. 2 and 3 show the numbers used to assign the carbons present in the functionalized titania and immobilized titania with AT and ^{13}C NMR for TiPCl and TiAT, respectively.

The ^{13}C NMR spectrum of the TiPCl exhibits three well-defined peaks at 14.5, 31.4 and 52.8 ppm, which were attributed to the carbons 1–3, respectively (Fig. 2). These signals appear at 11, 27.7 and 45.6 ppm in the spectrum of TiAT, while the other three distinct peaks at 86.4, 127 and 166.5 ppm correspond to the aromatic carbons 5, 6 and 4, respectively. The carbon atom of the methoxy group (–OCH_3) of the silylant chemically bonded to titania does not appear in the spectra in Fig. 3, which can be explained by the hydrolysis of methoxy groups during washing with water [26].

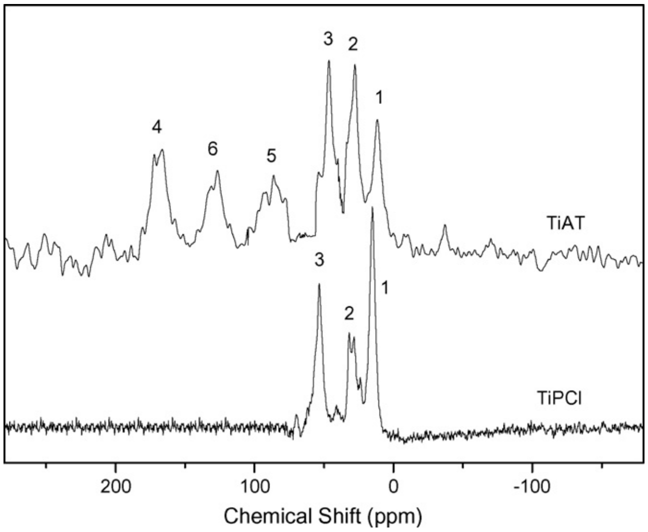


Fig. 3. Solid-state ^{13}C NMR spectra of TiPCl and TiAT.

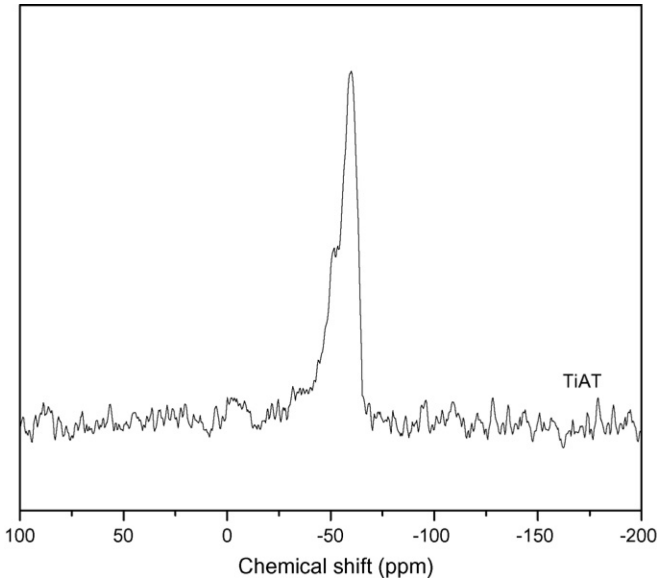


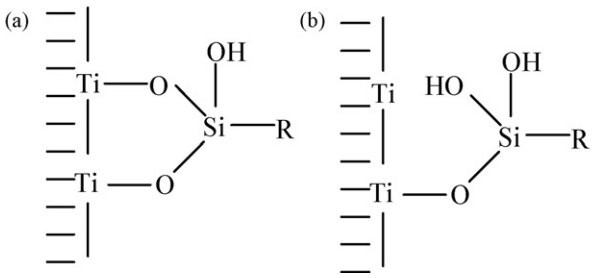
Fig. 4. Solid-state ^{29}Si NMR spectrum of TiAT.

The spectrum of the silicon nucleus in solid-state for the final catalyst is shown in Fig. 4. A well defined peak at −59 ppm is assigned to the T^3 [Si(OTi)$(OH)_2$R], where R is a carbon chain and the shoulder observed at −51 ppm is attributed to a T^2 structural unit [Si$(OTi)_2$(OH)R] [27]. Therefore, this spectrum confirms that the SiCl was bonded onto TiO_2 surface in two ways. The main one involves the immobilization of silylant agent by two covalent bonds and the other one requires only one covalent bond, as illustrated in Scheme 1.

3.2. Photocatalytic experiments

3.2.1. Activity of the photocatalysts

The catalytic properties of the titania and of the synthesized photosensitizers in the photodegradation of phenol used as a probe organic compound were investigated. Photocatalytic assays were conducted in triplicate, showing good reproducibility of measurements. An excellent correlation was observed between phenol concentrations obtained from UV–vis and organic carbon content studies. The experiments using 15 mg L^{-1} phenol solutions with bare titania and with the photosensitizers TiAT and TiATPd, stirred continually for 3 h without irradiation in different pH values, revealed that the phenol degradation increased slightly as a function of time. On the other



Scheme 1. Titania support bonded with silylant agent by two covalent bonds (a) and by only one covalent bond (b).

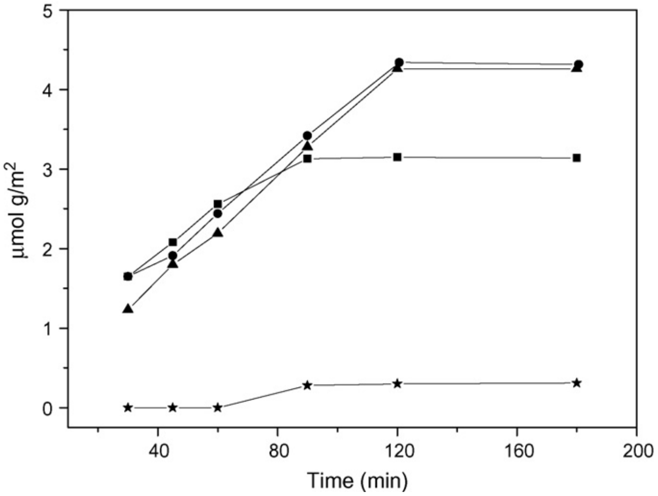


Fig. 5. Degraded quantity of phenol per specific surface area of catalyst (μmol g/m^2): TiO_2 (■), TiAT (▲) and TiATPd (●), and without catalyst (⋆) as a function of time under the conditions of: pH 3.0, 15 W black light.

hand, when these solutions were irradiated with black light for the same length of time, a pronounced increase of phenol degradation was observed, irrespective of pH.

Figs. 5–7 depict the degraded quantity of phenol per specific surface area of catalyst (μmol g/m^2). A set of control blank data, i.e., in the absence of catalysts, is also presented.

An analysis of these figures indicates that the photosensitizer TiATPd invariably presented higher activity than TiAT, regardless of pH and reaction time. In addition, after 90 min of reaction, the TiATPd displayed the highest activity in the entire range of pH studied. However, in shorter reaction times, titania exhibited higher activity than the other photocatalyts at pH 3.0 and 5.0, although its activity was consistently the poorest at pH 9.0.

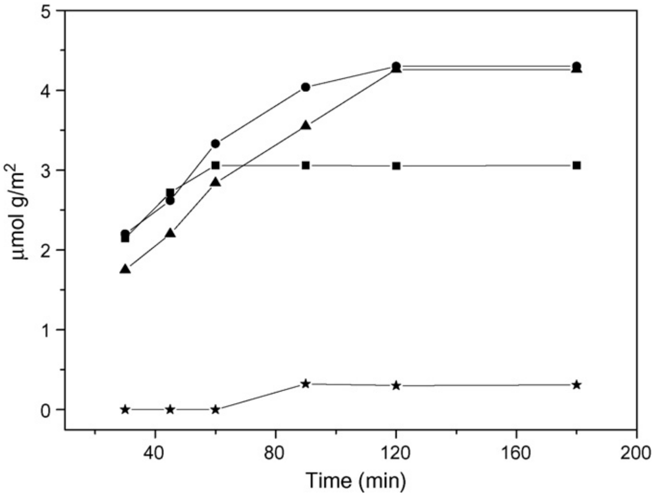


Fig. 6. Degraded quantity of phenol per specific surface area of catalyst (μmol g/m^2): TiO_2 (■), TiAT (▲) and TiATPd (●), and without catalyst (⋆) as a function of time under the conditions of: pH 5.0, 15 W black light.

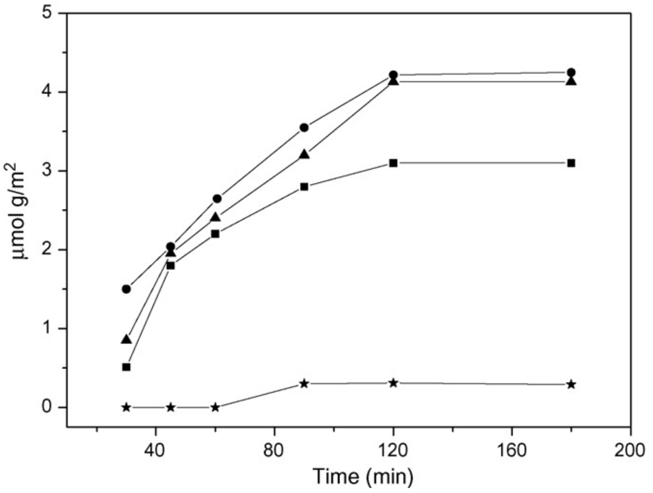


Fig. 7. Degraded quantity of phenol per specific surface area of catalyst (μmol g/m^2): TiO_2 (■), TiAT (▲) and TiATPd (●), and without catalyst (⋆) as a function of time under the conditions of: pH 9.0, 15 W black light.

The influence of pH on the photoactivity of catalysts can be explained by the fact that the pH of the aqueous solution affects TiO_2 significantly, including the charge of the particle and the size of the aggregates it forms. The pH at which the surface of an oxide is uncharged is defined as the Zero Point Charge (pH_{zpc}), which is around 7 for TiO_2. Above and below this value, the catalyst is negatively or positively charged in accordance with:

$$-TiOH_2{}^+ \leftrightarrow -TiOH + H^+ \tag{4}$$

$$-TiOH \leftrightarrow -TiO^- + H^+ \tag{5}$$

The equilibrium constants of these reactions are $pK_{TiOH_2{}^+} = 2.4$ and $pK_{TiOH} = 8.0$, the abundance of all the species as a function of pH: $-TiOH \geq 80\%$ when $3 < pH < 10$; $-TiO^- \geq 20\%$ if $pH > 10$; $-TiOH_2{}^+ \geq 20\%$ when $pH < 3$. Under these conditions, the photocatalytic degradation of the ionizable organic compounds is affected by the pH [7]. AT is known to protonate in acid medium, so the synthesized photocatalysts are protonated at pH 3.0 as well. Hence, substrate–catalyst repulsion occurs, which is probably responsible for the lower catalytic activity of the modified catalysts at this pH. The absence of this repulsion at pH 5.0, in which the surface of the photocatalyst is neutral, explains the superior photocatalytic activity (Fig. 6). With regard to the bare titania, the lowest photocatalytic activity was found to occur at pH 9.0. This may be explained by the fact that, at such an alkaline pH, the majority of titania species are in the negative form ($-TiO^-$), while the majority of phenol species ($pK_a = 9.89$) are in the form of PhO^-, giving rise to repulsion and thus diminishing the activity. The possible presence of carbonates and bicarbonates at this pH, which are oxidized by hydroxyl radicals on the TiO_2 surface, can be considered as an additional factor for the low activity of bare titania at this pH. On the other hand, the synthesized photocatalysts presented higher activity than titania at pH 9.0. Since the acidic hydrogens on the catalyst surface do not ionize to form $-TiO^-$ because of the reaction with organic groups, there is a decrease in substrate–catalyst repulsions, increasing the photoactivity. It was also found that the TiATPd photosensitizer invariably presented higher phenol degradation than TiAT in the same reaction time and at any pH studied, indicating that the metal-sensitizer charge transfer is a preponderant factor [8,28].

The quantity of palladium present in solution after the photodegradation process using TiATPd as photocatalyst could not be analyzed because of its possible lixiviation. The signal acquired was below the quantification limit for the FAAS technique (0.50 μg L^{-1}).

3.2.2. Mechanism

The results indicated that the photocatalytic activity of the TiATPd catalyst was consistently higher than that of the TiAT for phenol degradation.

Although the detailed mechanism of TiO_2 photocatalyzed reactions differs from one pollutant to another, it has been widely recognized that superoxide and, specifically, $^{\bullet}OH$ hydroxyl radicals, act as active reagents in the mineralization of organic compounds [29]. These radicals are formed by scavenging of the electron–hole pair by molecular oxygen and water, Eqs. (6)–(10).

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{cb} + h^+_{vb}) \quad (6)$$

$$O_2 + e^-_{cb} \rightarrow {}^{\bullet}O_2{}^- \quad (7)$$

$$H_2O + h^+_{vb} \rightarrow {}^{\bullet}OH + H^+ \quad (8)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (9)$$

$$H_2O_2 + {}^{\bullet}O_2{}^- \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (10)$$

It is also well established in the literature that the photosensitization of TiO_2 occurs by the initial excitation of the sensitizer, Eq. (11), followed by electron injection into the semiconductor conduction band, Eq. (12) [30–32].

$$\text{Sens} + h\nu \rightarrow {}^{*}\text{Sens} \quad (11)$$

$$^{*}\text{Sens} + (\text{SC}) \rightarrow \text{Sens}^{+}e^-_{cb}(\text{SC}) \quad (12)$$

Although we did not conduct experiments to confirm the role of the Pd(II) 2-aminothiazole as a sensitizer, this would be a possibility. In that case, the electrons of the conduction band could be reduced from Pd(II) to Pd(I) in the system studied here, so that

$$TiO_2[\text{Pd(II)Sens}] + e^-_{cb} \rightarrow TiO_2[\text{Pd(I)Sens}] \quad (13)$$

In addition, our results showed a beneficial effect on the photoreactivity of TiATPd towards phenol, which could probably be attributed to a cooperative mechanism. Thus, the two components of the photocatalyst, Pd(II)Sens and TiO_2 semiconductor, would contribute to the generation of active species in the mineralization of the organic material [8,28,33]. Subsequently, therefore, the reoxidation of Pd(I) to Pd(II) not only by O_2 but also by H_2O_2, produced in solution (Eqs. (6–10)) in the presence of sensitizer, could significantly improve the kinetics of the process (Eqs. (14) and (15)).

$$TiO_2[\text{Pd(I)Sens}] + O_2 \rightarrow TiO_2[\text{Pd(II)Sens}] + {}^{\bullet}O_2{}^- \quad (14)$$

$$TiO_2[\text{Pd(I)Sens}] + H_2O_2 \rightarrow TiO_2[\text{Pd(II)Sens}] + {}^{\bullet}HO + OH^- \quad (15)$$

Another possible factor for the increase in the activity involves the spatial separations of the charge carriers in the modified catalyst. Pd(II)Sens could provide efficient traps for conduction band electrons, indirectly accelerating the oxygen reduction [33]. Be that as it may, $^{\bullet}O_2{}^-$ species would be generated, which are essential for inducing the formation of $^{\bullet}OH$ radicals, whose insertion into C–H bonds ultimately leads to the complete mineralization of the organic substrate (Eq. (16)).

$$\text{Phenol} + {}^{\bullet}OH \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (16)$$

4. Conclusions

The synthesized TiATPd was found to be able to anchor onto the surface of titania via silyl linkage, which enables electronic coupling between the photosensitizer and TiO_2 and could mediate the injection of electrons from the photosensitizer to the conduction band of titania upon photoexcitation. TiATPd proved to be a more efficient catalyst than TiAT for phenol degradation, irrespective of pH, showing a significant beneficial effect because of metal. At long reaction times, the bare titania presented the poorest photocatalytic activity in the entire range of pH studied.

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