PHOTOCATALYSIS: NEW HIGHLIGHTS FROM JEP 2013

Visible-light driven oxidation of gaseous aliphatic alcohols to the corresponding carbonyls via TiO$_2$ sensitized by a perylene derivative

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Abstract Sensitized P25 TiO$_2$ was prepared by wet impregnation with a home-prepared perylene dye, i.e., N,N′-bis(2-(1-piperazino)ethyl)-3,4,9,10-perylene-tetracarboxylic acid diimide dichloride (PZPER). Energy levels of PZPER were found to be compatible with those of TiO$_2$ allowing fast electron transfer. The obtained catalyst has been characterized and used in the gas-phase partial oxidation of aliphatic primary and secondary alcohols, i.e., methanol, ethanol, and 2-propanol. The reaction was carried out under cut-off ($\lambda >$ 400 nm) simulated solar radiation in O$_2$ atmosphere. The perylene derivative allowed a good absorbance of visible radiation thanks to its low optical energy gap (2.6 eV) which was evaluated by cyclic voltammetry. The optimal organic sensitizing amount was found to be 5.6 % *w/w* in terms of yield in carbonyl derivatives. Moreover, no change in reactivity/selectivity was observed after 10-h irradiation thus confirming the catalyst stability. Yields into formaldehyde, acetaldehyde, and acetone were 67, 70, and 96 %, respectively. No significant amounts of organic byproducts were detected but for methanol oxidation, whereas a minor amount of the substrate degraded to CO$_2$.

Keywords Perylene-sensitized TiO$_2$ · Visible light photocatalysis · Aliphatic alcohol oxidation

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Introduction

Titanium dioxide is the most used photocatalyst among several inorganic semiconductors due to its high photostability, activity, and low cost (Serpone and Pelizzetti 1989; Palmisano et al. 2007; Augugliaro et al. 2012; Wang et al. 2010a, 2010b; Scanlon et al. 2013). However, the wide band gap of TiO$_2$ (ca. 3.0 and 3.2 for pure rutile and anatase, respectively) makes this semiconductor absorb in the ultraviolet region, that represents only 2–3 % of solar radiation. Its modification, in order to attain visible absorption, is thus highly desirable (Youngblood et al. 2009; Qin et al. 2011; Mele et al. 2002).

Photocatalysts active under visible light irradiation allow the free, clean, and renewable solar energy to be used in the preparation of many organic compounds (Augugliaro et al. 2011; Parrino et al. 2008). Narrowing TiO$_2$ band gap energy can be, for instance, achieved via doping by metal and non-metal atoms (Park et al. 2013; Yurdakal et al. 2012; Hashimoto et al. 2011; Dai et al. 2009).

A different approach is represented by TiO$_2$ sensitization (Palmisano et al. 2008; Parrino et al. 2012), that does not produce an intrinsic modification of the photocatalyst band gap as in the case of metal or non-metal doping, indeed introducing a visible light-absorbing intermediate species. The working principle of sensitized-TiO$_2$ photocatalysis is basically the following: a chromophoric species acting as the sensitizer absorbs visible radiation and gives rise to the energetic promotion of an electron; the latter one is injected into the conduction band of TiO$_2$, thus producing an efficient redox reaction by following different routes. Previous mechanistic works showed that the fate of the produced charge carriers represents the key step of the whole photocatalytic process, and the presence of a sensitizer positively affects their lifetime by hindering hole–electron recombination (Wang et al. 2010a, 2010b; Palmisano et al. 2008). Bearing in mind

that the lowest unoccupied molecular orbital (LUMO) energy level of the organic sensitizer must be less negative than the conduction band edge of TiO_2 to make electron transfer possible, the consequent enhanced hole–electron spatial separation is another important beneficial effect of sensitizing TiO_2.

The selective oxidation of aliphatic alcohols to corresponding carbonyls is one of the most widespread and important reactions in organic chemistry and is applied to the manufacture of fine chemicals such as perfumes and food additives (Pillai and Sahle–Demessie 2002; Muggli and Falconer 1998). Moreover, the conversion of low molecular weight alcohols into useful organic intermediates is highly required. Accordingly, ethanol acts as the raw material for the production of acetaldehyde through oxidative dehydrogenation and for the production of acetic acid; the former process indeed allows the critical introduction of bioethanol in several production cycles. Photocatalytic oxidation of ethanol has been studied under UV-LED radiation in gas phase (Murcia et al. 2012a, 2012b) whereas allylic alcohols such as geraniol and trans-2-penten-1-ol have been oxidized in various media, along with primary alcohols such as citronellol and 1-pentanol, by using TiO_2-based photocatalysts (Pillai and Sahle–Demessie 2002).

Recently, Nasalevich et al. (2012) investigated the activity of CdS for the partial oxidation of ethanol and isopropanol under visible light in gas phase reactors in oxygen atmosphere. The used CdS catalysts were prepared through a two-step synthesis: (1) reaction between $CdCl_2$ and NaOH and (2) exchange of hydroxide ions of $Cd(OH)_2$ intermediate with S^{2-} ions to form CdS. During the oxidation of ethanol and isopropanol, only acetaldehyde, in the former case, and acetone, in the latter one, were detected among gas phase reaction products. Catalyst activity was found to grow by increasing the S/Cd molar ratio in precursor solutions and reached its maximum value at 2:1.

Hereby, we report one of the very first examples of visible light photocatalytic selective oxidation of aliphatic alcohols in gas phase, carried out by irradiating with a solar simulator coupled to a cut-off ($\lambda > 400$ nm) filter. The employed catalyst was the most widely used TiO_2, i.e., P25, sensitized by a home-prepared perylene derivative, i.e., N,N′-bis(2-(1-piperazino)ethyl)-3,4,9,10-perylene-tetracarboxylic acid diimide dichloride (PZPER) (Donati et al. 2009). It should be underlined that perylene derivatives have been poorly studied as sensitizers in photocatalytic reactions (Kim et al. 2010): in particular 3,4,9,10-perylene-tetracarboxylic diimide has been used to sensitize TiO_2 for application in water remediation in order to degrade methylene blue and formaldehyde. Nevertheless, energy levels of perylene derivatives are often compatible with those of TiO_2. In the present work, we characterized energy levels of PZPER and investigated the electronic features of PZPER/TiO_2 by means of UV-visible diffuse reflectance spectra. Furthermore, the influence of

sensitizer amount on TiO_2 was studied. Finally, three different aliphatic alcohols—methanol, ethanol, and 2-propanol—have been oxidized to the corresponding carbonyls and their yields were calculated.

Materials and methods

Preparation and characterization of PZPER and PZPER/TiO_2

Perylene-3,4,9,10-tetracarboxydianhydride (5 g, 12.75 mmol) was dissolved in 100 mL of 1-(2-amino-ethyl)piperazine at 160 °C and stirred for 22 h. After cooling down to room temperature, the solution was treated with 500 mL of 2-M HCl. The resulting dark violet solution was stirred for 12 h. The reaction product was precipitated as chloride salt in acetone, separated by filtration, washed thoroughly with distilled water, until the pH of the washings became neutral, and finally dried. A deep red solid (6.5 g, 9.6 mmol, yield: 75.6 %) was recovered and characterized by UV–Vis and FT-IR for identification purposes by comparison with literature data (Donati et al. 2009).

PZPER/TiO_2 catalysts were prepared by wet impregnation by adding 1 g of TiO_2 into 20-mL PZPER aqueous solution. The suspension was treated in an ultrasonic bath for 0.5 h and then left under stirring overnight. Finally, it was subjected to a freeze-drying process in order to get rid of water by means of a CHRIST Alpha 1–2 LD Plus (temperature and pressure set at −76 °C and 0.03 mbar, respectively). Three different catalysts were prepared with PZPER loadings equal to 0.056, 0.56, and 5.6 % w/w with respect to TiO_2.

Cyclic voltammetry measurements were made in a three-electrode electrochemical cell by a CH Instruments Electrochemical Analyzer. The reference electrode was a non-aqueous Ag/Ag$^+$ (containing a 0.01-M solution of tetrabutylammonium perchlorate in acetonitrile) provided by AMEL. The counter electrode was a platinum foil (surface equal to ca. 0.5 cm^2). In order to obtain the working electrode, the PZPER was deposited as thin film by dip coating of an FTO-functionalized glass electrode (Pilkington TEC15) into a PZPER organic solution (chloroform-methanol 50 % v/v) at a rate equal to 60 cm min^{-1}. The non-conductive glass side was carefully cleaned with methanol soon after deposition. The electrolytic solution was made of 0.1-M lithium perchlorate in anhydrous acetonitrile. The cyclic voltammetric measurements were made in different ranges of potential, operating both in reduction and in oxidation, with a scan rate of 50 mV s^{-1}. Before each voltammetry, the electrolytic solution was stirred by a magnetic stirrer and bubbled with nitrogen for 0.5 h to strip the dissolved oxygen.

UV-visible spectra in the 200–800-nm range were obtained in absorbance mode for solutions and in reflectance mode for powders. A Shimadzu UV-2401 PC instrument was used and

diffuse reflectance spectra (DRS) were recorded by using BaSO$_4$ as the reference. The DRS spectra of pure PZPER were recorded by mixing 50 mg of PZPER with 2 g of BaSO$_4$, whereas those of sensitized TiO$_2$ were recorded by using the pure powders. FT-IR spectroscopy was performed by means of a FTIR 8400 Shimadzu.

Photocatalytic setup and analytical techniques

Photocatalytic runs were performed in a Pyrex-made batch cylindrical gas-seal photoreactor (volume 0.12 L, external diameter 8.5 cm, external height 2.5 cm), equipped with a silicon/teflon septum used in order to withdraw samples in the course of reaction. One-gram catalyst was dispersed in the photoreactor and the environment was saturated by oxygen by feeding the reactor for 0.5 h. Afterward, a certain amount of liquid reagent (methanol, ethanol, or 2-propanol) was introduced in the reactor by means of a 50-μL Hamilton microsyringe in order to get a concentration of 1 mM. Then, 0.5 h were waited to get substrate complete evaporation and reach adsorption-desorption steady state equilibrium conditions, indicated by a stable concentration of the alcohol in the gas phase. A Solarbox (Xenon lamp of 1,500 W) was employed as irradiation source, 1-M nitrite aqueous solution ensured cut-off of 99 % UV radiation (λ<400 nm) and hindered IR radiation to pass through producing a significant reactor overheating. The 450–950-nm radiance reaching the reactor upper surface was equal to 850 W/m^2. Radiation was measured with 315–400 and 400–900-nm probes by using a Delta Ohm DO 9721. Reactor temperature was ca. 40 °C. Samples of gas (500 μL) were withdrawn by using gas-tight syringes at fixed-time intervals. All the organic species were monitored by means of a GC-17A Shimadzu GC equipped with a methyl siloxane (30 m×320×0.25 μm) HP-1 Hewlett-Packard column kept at 40 °C and a flame ionization detector. Helium was used as carrier gas. Carbon dioxide was measured by a Hewlett-Packard 6890 GC equipped with a 60/80 Carboxen 1000 Supelco column and a thermal conductivity detector. The accuracy of GC measurements (maximum error ca. 4 %) was verified by multipoint calibration of the analyzed molecules. For checking the repeatability of the photoreactivity experiments, each run was carried out two times, by achieving a maximum difference in yield of ca. 3 %.

Results and discussion

Cyclic voltammetric and spectrophotometric measurements

The as synthesized PZPER was properly characterized in order to get information about its ability to absorb visible light and inject electrons into the conduction band of TiO$_2$ eventually promoting reactivity under visible irradiation.
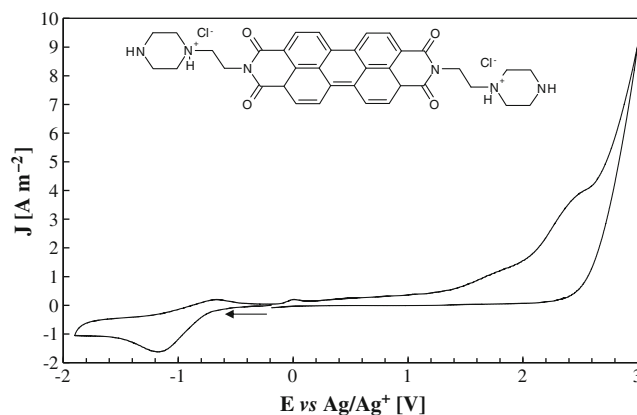

Fig. 1 Cyclic voltammetry of *PZPER* film in *LiClO*$_4$ deaerated anhydrous acetonitrile solution. The *arrow* denotes the direction of the potential scan

Cyclic voltammetric analyses were performed by using a PZPER thin film deposited by dip-coating in the range between −1.8 and 3.0 V vs. Ag/Ag$^+$ non-aqueous reference electrode. Figure 1 shows a representative curve where the current density is plotted as a function of the potential. The reduction and oxidation potentials were calculated from $E_{\mathrm{red1/2}}$ (i.e., the mediated anodic and cathodic peak potentials) and the onset oxidation potential, respectively, and hence correlated to highest occupied molecular orbital (HOMO) and LUMO levels confidently, since the experiments were carried out in the absence of O$_2$ and water in order to exclude a degradation of the organic species. The following relationships were applied according to the relevant literature (see for instance Deng et al. 2012):

$$E_{\mathrm{LUMO}} = \left[-\left(E_{\mathrm{red1\,2}} + E_{\mathrm{Ag\,Ag+}} \right) - 4.5 \right] eV \qquad (1)$$

$$E_{\mathrm{HOMO}} = \left[-\left(E_{\mathrm{ox}} + E_{\mathrm{Ag\,Ag+}} \right) - 4.5 \right] eV \qquad (2)$$

where $E_{\mathrm{Ag/Ag+}}$ is the potential of Ag/Ag$^+$ vs. NHE, that is equal to 0.36 V.
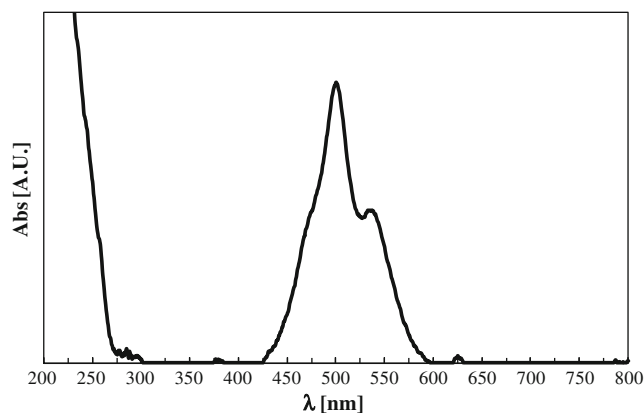

Fig. 2 Absorbance spectrum of *PZPER* in aqueous solution
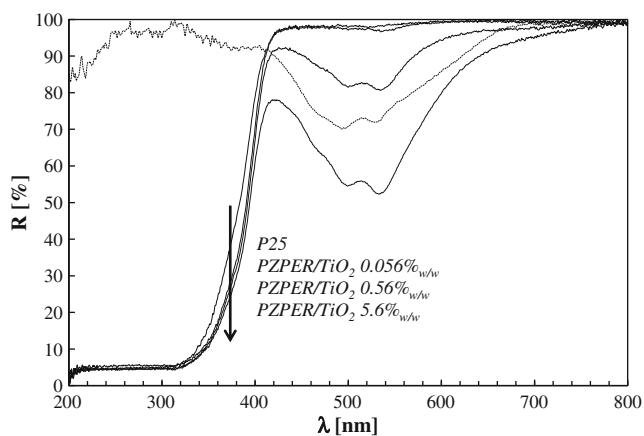
Fig. 3 Diffuse reflectance spectra of *PZPER* (*dotted line starting up-left*) and *PZPER/TiO2* at different loadings

Based on cyclic voltammetry results, the HOMO and LUMO levels of PZPER are −6.5 and −3.9 eV, so that the energy gap of PZPER is equal to 2.6 eV. This energy gap corresponds to a wavelength of ca. 1,240/2.6=477 nm. This value is in good agreement with literature data (Donati et al. 2009) and with the absorbance spectra of PZPER in aqueous solution reported in Fig. 2. Figures 1 and 2 clearly show that PZPER is able to absorb visible light and can undergo promotion of electrons from HOMO to LUMO level under irradiation at wavelengths in the visible light range.

TiO2 sensitized by PZPER was prepared by wet impregnation in water followed by freeze-drying in order to avoid thermal treatments that could generate modifications in PZPER/TiO2 structure and—at the same time—to be aware of the exact amount of PZPER adsorbed on TiO2 surface. The loading amounts with respect to TiO2 were selected in the wide 0.056–5.6 % w/w range in order to guess amounts around the typical sensitizing percentages reported in literature (Wang et al. 2007). The wet impregnation was carried out in water thanks to the high solubility of PZPER (that is a chloride salt) that can be thus safely processed. The adsorption of the dye on TiO2 may occur via interaction of the pyridyl nitrogen lone pairs on the Lewis acidic sites of TiO2. As argued by Ooyama et al. (2010) on the basis of the IR spectra of similar organic molecules adsorbed on TiO2 particles, electron injection can take place efficiently from the pyridine ring to TiO2 conduction band through the strong coordination bonding rather than

the hydrogen bonding between the pyridine ring of the dye and the TiO2 surface. The adsorption mode is not trivial since it affects the electron transfer from the LUMO level of PZPER to the conduction band (CB) of TiO2. Sharing electrons by means of chemical bonds or even weaker interactions is indeed crucial for the effectiveness of TiO2-PZPER interaction and then for the photocatalytic efficiency of the hybrid system.

Figure 3 shows the UV–Vis diffuse reflectance spectra of PZPER/TiO2 catalysts at different PZPER loadings: the spectra can be roughly divided in two areas of absorbance at $\lambda >$ 400 nm and at $\lambda <$ 400 nm, where PZPER and TiO2 absorb, respectively. Moreover, the sensitized catalysts absorb much more in the visible region by increasing PZPER amount. The difference is evident at $\lambda >$ 400 nm, although a certain improvement in the absorption ability at $300 < \lambda < 400$ nm can be seen for PZPER/TiO2 0.056 % w/w with respect to P25 TiO2, remaining unaltered for higher PZPER loadings.

Photocatalytic tests

Photocatalytic tests were firstly carried out by oxidizing 2-propanol. No reactivity was observed in the absence of light, catalyst, or oxygen. Moreover, the use of solids such as SiO2 and Al2O3, as well as pure PZPER, did not give rise to any activity even under irradiation. We can thus conclude that the oxidation of aliphatic alcohol is a heterogeneous photocatalytic reaction and PZPER alone is not able to oxidize the alcohols. In fact, its small energy gap favors electron–hole recombination and the HOMO energy level is not positive enough to afford alcohol oxidation.

Both bare and PZPER-loaded P25 TiO2 were used. Table 1 reports the results of oxidation of 2-propanol to acetone in terms of initial rate of formation and maximum yield into acetone for the experiments performed on P25 TiO2 and on PZPER/TiO2 catalysts, by varying the PZPER loadings. Conversions are not reported since a significant amount (ca. 94 %) of 2-propanol adsorbs on bare and sensitized TiO2 in dark conditions and it is hence impossible to know the global amount of converted substrate.

By increasing PZPER loading, an increase in reaction rate is observed with a threefold gain with respect to bare TiO2 when using a 0.56 % loading. An increase of the maximum

Table 1 Initial rate and maximum yield of acetone production for different PZPER loading amount

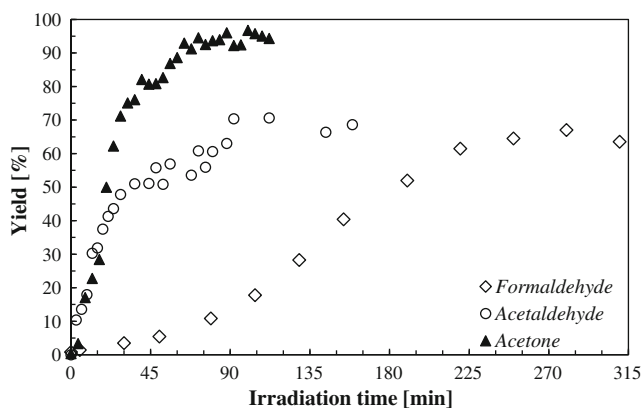| PZPER (% w/w)	$r_{0,\ formation}$ [mM min^{-1}]			Maximum yield (%)		
	First run	Second run	Third run	First run	Second run	Third run
0	0.0066	–	–	86	–	–
0.056	0.00671	0.00673	0.0067	88	88	89
0.56	0.0196	0.0200	0.0198	95	94	94
5.6	0.0183	0.0180	0.0181	96	95	96

Fig. 4 Yield into formaldehyde, acetaldehyde, and acetone by oxidation of methanol, ethanol, and 2-propanol, respectively (PZPER loading: 5.6 % w/w)

yield in carbonyl derivatives is also afforded from 86 to 96 %. These figures were calculated by dividing the product concentration by the initial alcohol concentration.

This suggests an improvement in the reactivity of the TiO_2 in the visible range thanks to the improved absorption of visible light and the reduction of electron–hole recombination. A further increase of PZPER loading from 0.56 to 5.6 % w/w does not result in any advance in reactivity but only in a slight enhanced selectivity. This is probably because the highest contact surface and thus electronic exchange between TiO_2 and PZPER is already reached with the 0.56 % sample. Not surprisingly, P25 TiO_2 is reactive since it absorbs a certain fraction of light even at $\lambda > 400$ nm, as also previously shown in literature (Jiang et al. 2008; Triantis et al. 2012). Thus, the activity under visible light can be attributed to the excitation of rutile (absorption threshold ca. 414 nm). Notably, charge transfer between the two crystallite phases can also occur, allowing for photocatalytic redox events on anatase surface, although the threshold of anatase is ca. 388 nm (Yang Teoh
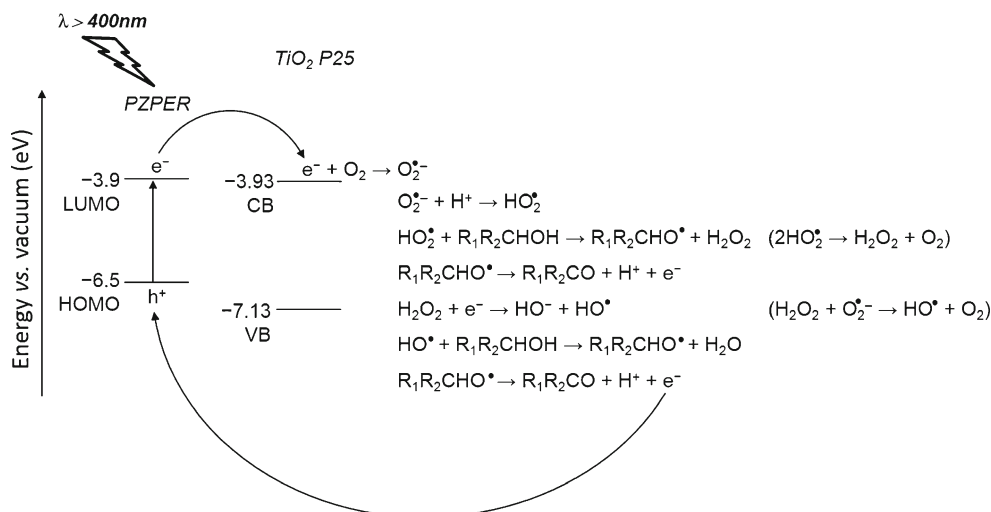
et al. 2007). It should be underlined that the reported threshold values for anatase and rutile can undergo small variations by changing the catalyst samples; however, rutile—unlike anatase—generally shows a certain absorption in the visible range. In order to better understand the results reported in Table 1, a rough calculation of the amount of PZPER corresponding to an adsorbed monolayer was carried out as described in the following. The Connolly molecular area (Connolly 1983) of PZPER was evaluated by the software ChemBio3D Ultra, and was equal to 534 $Å^2$. The specific molecular surface per weight unit can thus easily be found by multiplying the molecular surface by the Avogadro constant and dividing by PZPER molecular weight. It is equal to 4,660 m^2/g. Now, by considering that P25 TiO_2 specific surface area equals to 50 m^2/g (Ohno et al. 2001), the surface corresponding to a monolayer of PZPER adsorbed onto TiO_2 was calculated as 1.07 % w/w by dividing the specific surface area of PZPER by that of TiO_2. This result is in good agreement with experimental results in Table 1, showing the highest reaction rate for 0.56 % w/w, that is the value closest to 1.07 % w/w.

The partial oxidation of three different alcoholic substrates, i.e., methanol, ethanol, and 2-propanol, was performed by using best performing catalyst yielding 96 % into acetone, according to Table 1.

The yields to formaldehyde, acetaldehyde, and acetone with respect to time are shown vs. irradiation time in Fig. 4. As can be easily seen, the maximum yields obtained are equal to 67, 71, and 97 % in formaldehyde, acetaldehyde, and acetone, respectively.

The samples analyzed by gas chromatography showed no evidence of formation of byproducts in the case of ethanol and 2-propanol oxidation: only traces of CO_2 were detected. However, methanol oxidation produced some other unidentified intermediates and resulted to be much slower than the

Scheme 1 Reaction mechanism for aliphatic alcohols to the corresponding carbonyls ($R_i = H, CH_3$)

others. It should be underlined that the carbon balance cannot be satisfied in ethanol and methanol oxidation likely because a part of alcohol and/or aldehyde remained adsorbed onto the catalyst surface. This hypothesis is supported by the initial strong adsorption of alcohols onto the catalyst surface occurring even in dark conditions (94, 75, and 97 % for 2-propanol, ethanol, and methanol, respectively). Notably, the maximum concentrations of acetone, acetaldehyde, and formaldehyde are stable during a prolonged time and these species undergo a significant overoxidation only after an extended irradiation time, thus facilitating their possible recovery from the reaction environment.

Photocatalytic tests were performed on the prepared PZPER/TiO$_2$ samples in three different consecutive runs (ca. 10-h irradiation) in order to evaluate the stability during time (see Table 1). We have indeed observed that the reactivity of the catalysts has not changed in the three runs, with a complete reproducibility (maximum deviation: 5 %). Hence, we can conclude that even in the presence of a slight degradation of PZPER during irradiation, the sensitized catalyst resulted to be stable in activity for a prolonged time. The similar UV–Vis absorption spectra of PZPER/TiO$_2$ recorded before and after photocatalytic runs are also a proof of catalyst stability.

On the basis of (1) previous studies regarding the application of TiO$_2$ sensitized by organic molecules in photocatalytic oxidation (Wang et al. 2007), (2) the reported mechanisms of alcohol to carbonyl compounds photocatalytic oxidation (Augugliaro et al. 2008; Zhang et al. 2009), and (3) the experimental data collected in the present study, the following general reaction mechanism has been hypothesized (Scheme 1).

Absorbance of visible light by PZPER produces an electron promotion from HOMO to LUMO level. Since LUMO level (−3.9 eV vs. vacuum) is higher than the CB level of TiO$_2$ P25, –3.93 eV vs. vacuum (see Marcì et al. 2013), electrons can be easily injected from the organic sensitizer to the CB of TiO$_2$, most likely, via pyridyl nitrogen lone pairs. Recombination can certainly occur, with the electron in the semiconductor's CB going back to the organic dye (electronic recombination). These events are clearly drawbacks hindering to reach high-process efficiencies. Nevertheless, in the presence of O$_2$, such as in the environment of our reaction, the CB electrons can also react with surrounding electrophilic O$_2$ molecules, giving rise to O$_2^{\bullet-}$ radicals. These are hypothezised to react with an H$^+$ coming from Ti-OH surface acidic sites (Zhang et al. 2009) giving rise to HO$_2^{\bullet}$. The latter radical is certainly able to oxidize an alcohol molecule by abstraction of an H$^{\bullet}$ and the subsequent production of hydrogen peroxide. The as-formed alkoxy radical is hence transformed into the carbonyl species (aldehyde or ketone from primary and secondary alcohols, respectively) by the loss of an H$^+$ that can interact with TiO$_2$ surface basic sites (alternatively HO$_2^{\bullet}$ can give rise to H$_2$O$_2$ and O$_2$). The loss of H$^+$ occurs concurrently to the release of

an electron that can reduce the previously produced hydrogen peroxide, thus generating OH anions and radicals. OH radicals—that can form also by reaction of H$_2$O$_2$ and O$_2^{\bullet-}$—in turn, are able to oxidize another alcohol molecule again by H$^{\bullet}$ abstraction and water production, followed by production of a carbonyl group. The electron produced at the end of the cycle can replace the one lost by PZPER at the beginning of the process.

Conclusions

TiO$_2$ P25 sensitized by a perylene derivative (PZPER) was prepared by wet impregnation followed by freeze-drying. The measured PZPER energy levels (HOMO −6.5 eV; LUMO −3.9 eV) were found to be compatible with valence and conduction band of TiO$_2$ and this can explain the efficient electron transfer between PZPER and TiO$_2$. The obtained composite catalyst was active under visible radiation, and it was able to efficiently oxidize methanol to formaldehyde, ethanol to acetaldehyde, and 2-propanol to acetone, with yields ranging from 67 to 96 %. An increase of sensitizer amount over 0.56 % w/w produced only a small improvement in yield. All these reactions were carried out in oxygen atmosphere in a gas-solid regime, without the use of any co-solvent or additive and simulated solar light was applied in order to demonstrate the potentiality of this green process. By concluding, we have showed the possibility to use an easily prepared perylene-sensitized TiO$_2$ under cut-off ($\lambda > 400$ nm) simulated solar radiation in O$_2$ atmosphere to efficiently oxidize primary and secondary alcohols to the corresponding carbonyls. This study encourages important applications, as for instance, the introduction of bioethanol in the industrial chain of commodities and fine chemicals production. No significant organic byproducts have been detected in the oxidation of 2-propanol and ethanol and the catalyst showed significant time stability.

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