



Full Length Article

Enhanced methylene blue photodegradation with propylene carbonate as a solvent

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ABSTRACT

The role of water in the TiO₂-based photocatalytic phenomenon is not yet fully understood. The photocatalysis of methylene blue dissolved in propylene carbonate and different concentrations of water was studied. It was observed that the photocatalytic activity of TiO₂ (P25 from Evonik) peaks when propylene carbonate solvent is used with minute amounts of water; the maximum photodegradation rate was *ca.* 6.5 times higher than when just water solvent was used. The conventional interpretation of the methylene blue photooxidation intermediated by free radical OH[·] cannot explain these results. Alternately, the experimental results were interpreted based on the recently proposed “direct–indirect” (D-I) model and a mathematical model was successfully developed and fitted to the experimental results. Finally, new insights on the role of water in the photocatalytic phenomenon were withdrawn.

1. Introduction

Photocatalysis based on titanium dioxide anatase has attracted the attention of many researchers mainly due to its wide range of applications - photoabatement of atmospheric contaminants, water treatment and the inactivation of microorganisms both in suspension and on surfaces [1–3], among others. Titanium dioxide (TiO₂) is the most studied semiconductor in the field of photocatalysis. This interest on TiO₂ material was fueled by the pioneer work by Fujishima et al. [4] in 1972, who described for the first time the water splitting using a TiO₂ photoelectrode.

The anatase band gap is *ca.* 3.2 eV while the band gap of rutile is *ca.* 3.0 eV. Upon excitation with photons presenting energy higher than the band gap energy, electrons are injected from the valence to the conduction band, generating electron-hole pairs in the conduction and valence bands, respectively – Eq. (1). The photogenerated charges diffuse to the surface of the semiconductor particle where they promote redox reactions; holes may generate vacancies on TiO₂ surface or excited reduced species, while excited electrons normally react with oxygen to produce free radical O₂^{·-}. These are responsible for the photodegradation of organic compounds, where adsorbed water and oxygen have been described to play a critical role [5,6].

The mechanism of photodegradation has been thoroughly studied, and several pathways for the photodegradation of pollutants have been reported [7,8]. The most commonly assumed photodegradation

mechanism is based on Langmuir-Hinshelwood kinetic model, as described by Ollis and Turchi [6]:



where OH[·] is the hydroxyl radical, O₂^{·-} is the superoxide radical and S are the active centers of the photocatalyst. This model assumes that the oxidation reactions are intermediated by free radical OH[·], which is formed accordingly to Eq. (3). This assumption is based on studies of spin trapping and electron spin resonance (ESR) that evidence high concentrations of OH[·] radicals in photocatalytic systems [6]. Additionally, the pivotal role of hydroxyl radicals was also supported by the hydroxylated intermediates formed during the photodegradation of the studied compounds [6].

The role of water on photocatalysis has been questioned with increasing emphasis in recent years. Many authors showed that, in gas phase experiments, photocatalytic conversion increases with relative humidity only up to values of *ca.* 50% [9,10]; this effect was assigned to

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limitations on the UV light availability to form hydroxyl radicals [9,11]. Ângelo [12] reported recently a NO conversion for a dry feed (ca. -20°C of dew point) of $X_{\text{NO}} = 75.7\%$ and for a feed containing 25% of relative humidity (RH) of $X_{\text{NO}} = 82.4\%$, which is the maximum conversion as a function of the RH obtained by these authors. The same work indicates that the water-adsorbed monolayer on the TiO_2 particles is reached for a relative humidity of ca. 25%. If the main intermediate for the oxidation of NO was OH^{\cdot} , NO conversion for the dry feed would be rather small, see Eq. (3), which was not observed. Salvador and co-workers [13] also studied the influence of water on the photodegradation of benzene in a dispersion of TiO_2 (anatase sample) in anhydrous acetonitrile. These authors assigned the decrease in the photodegradation rate with the water concentration in liquid phase, to the water adsorption on the TiO_2 surface that hinders the chemical sorption of photogenerated intermediate species. This result, along with other studies reported in literature [14], question the role of hydroxyl radicals in photocatalysis or, otherwise, of Eq. (3).

Montoya and co-workers [15] argued strongly against the direct reaction of a photogenerated hole with adsorbed water or OH^- to form OH^{\cdot} . Besides questioning the participation of OH^{\cdot} radicals on the photodegradation mechanism, this work also studied the mechanism that leads to their formation and how these radicals interact with the reactant degradation [15]. These authors [15] suggested a novel pathway for the photocatalytic mechanism named direct-indirect model (D-I). Depending on the type of electronic interaction of the reactant with the semiconductor surface, the D-I model shows two different types of interfacial charge transfer mechanisms. For strong electronic interaction, D-I model assumes that photo-oxidation is mainly based in an interfacial direct transfer (DT) mechanism of photogenerated valence band free holes to adsorbed species to TiO_2 surface. On the other hand, for weak interactions between reactant and TiO_2 surface, the D-I model assumes an interfacial indirect transfer (IT) mechanism involving two successive steps: first species h_f^+ (surface free hole) are trapped by O_s^{2-} terminal oxygen ions of the TiO_2 surface leading to the generation of terminal $\text{O}_s^{\cdot-}$ radicals; next, surface trapped holes are isoenergetically transferred via tunneling to the adsorbed reactant, according to the Marcus-Gerischer model for adiabatic electron transfer at the semiconductor electrolyte interface [16]. Generally DT prevails over IT, although the contribution of both mechanisms can be comparable in some special cases [15]. Fig. 1 sketches the D-I model.

Salvador and co-workers [13] also analyzed the importance of oxygen on the photocatalytic phenomenon. The interaction between anatase nanoparticles and adsorbed O_2 was assessed by UV photo-induced oxygen isotopic exchange. The experimental results obtained showed that terminal 2-fold coordinated bridging oxygen ions ($>\text{O}_{\text{br}}^{2-}$) of the TiO_2 surface are exchanged with oxygen atoms of dissolved O_2 molecules. Furthermore, experimental evidences have recently been reported about the anaerobic mineralization of benzene dissolved in water using ^{18}O isotope-labeled titania (Ti^{18}O_2) as photocatalyst. The generation of $^{16}\text{C}^{18}\text{O}_2$ as mineralization product allowed to conclude that one-fold coordinated bridging oxygen radicals ($-\text{O}_{\text{br}}^{\cdot-}$), via inelastic trapping of holes (h_f^+) by terminal ($>\text{O}_{\text{br}}^{2-}$) ions, behave as structural oxygen species able to capture

electrons from adsorbed benzene on Ti^{18}O_2 via an adiabatic interfacial charge transfer mechanism [13]. Dillert et al. [17] and Ângelo et al. [12] also demonstrated the importance of oxygen for the photocatalytic phenomenon, showing that without oxygen there is no NO conversion. Thus, though several models have been proposed to explain the photocatalytic phenomenon, a definitive model has yet to be established.

In this work, the photocatalytic efficiency for the photodegradation of methylene blue was studied using propylene carbonate as solvent with different water concentrations. Additionally, a mechanism based on the D-I model is proposed for explaining the photodegradation of methylene blue and a mathematical model developed and fitted to the experimental results.

2. Materials and methods

2.1. Propylene carbonate

Propylene carbonate (Sigma-Aldrich, reagent grade) was used as a solvent for the photodegradation of methylene blue. The propylene carbonate was previously dehydrated heating at 120°C one and half hour while bubbling nitrogen from a cylinder (nitrogen 99.999% from Air Liquide). Methylene blue was dissolved in the propylene carbonate and used in the photocatalytic studies immediately after the dehydration process.

2.2. Titanium dioxide

Pristine and dehydrated anatase (P25 from Evonik) was used. The dehydration was conducted at 300°C during two hours under a nitrogen atmosphere. The sample was then stored in a container previously cleaned with nitrogen flow.

2.3. Methylene blue degradation

The photodegradation rate of methylene blue (MB) was followed by spectrophotometry. In a typical experiment, MB dye (10 and $18\text{ mg}\cdot\text{dm}^{-3}$) dissolved in an organic solvent – propylene carbonate – and photocatalyst (12.5 mg) were placed in a 50 mL cylindrical glass vessel. Under inert conditions (mixture was bubbled with a low nitrogen flow) and stirring, the photoreactor vessel was exposed to the UV irradiation produced by an ultraviolet (UV-A, highest emission at 365 nm) lamp with two 6 W black-light-blue bulbs (VL-206-BLB, Vilbert Lourmat, France); the lamp was positioned 10 cm away from the vessel (irradiance of $10\text{ W}\cdot\text{m}^{-2}$ measured at the reactant mixture surface using a UV radiometer (HD 2102.2, Delta/OHM, Italy)). Each experiment began putting the mixture during 30 min in the dark; the mixture was then illuminated for 15 min . Aliquots of ca. 2 cm^3 were centrifuged (Microcentrifuge, MiniStar silverline from VWR collection) for 5 min at 6000 rpm and the supernatant was analyzed in an UV-visible absorption spectrophotometer (Shimadzu UV-3600 UV-VIS-NIR spectrophotometer).

2.4. Quantification of hydroxyl radicals

The methodology used to assess the hydroxyl radicals formation was based on the works by Czili and Horváth [18], Marques et al. [19] and Louit et al. [20]. Briefly, photoluminescence technique (PL) was used for detecting hydroxyl radicals (OH^{\cdot}) produced during the photocatalysis reaction. Coumarin readily reacts with OH^{\cdot} radicals to produce a highly fluorescent sub product, 7-hydroxycoumarin (7HC), which shows a strong PL signal at 456 nm . After the correction of the coumarin PL signal, which is almost negligible, the 7-hydroxycoumarin fluorescence signal can be used to determine the OH^{\cdot} concentration. First, different concentrations of 7-hydroxycoumarin aqueous solutions were prepared and the photoluminescence signal was measured at 456 nm (PL signal of 7HC) to obtain the photoluminescence calibration

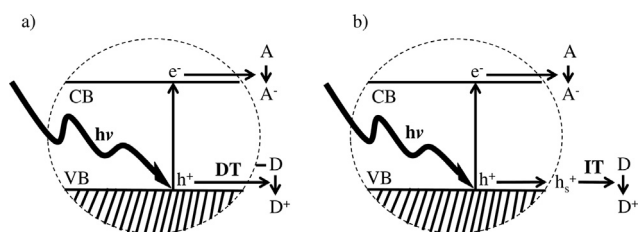


Fig. 1. Schematic of the direct-indirect model: (a) direct transition; (b) indirect transition. Adapted from [15] with permission. Copyright American Chemical Society 2014.

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