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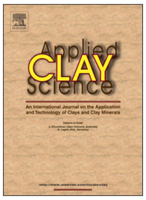

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Review article

Photocatalytic degradation of organic contaminants over clay-TiO_2 nanocomposites: A review

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ABSTRACT

Heterogeneous photocatalysis is an efficient, economical and environmentally friendly technology for removing organic contaminants from the aqueous environment. Titania is one of the most popular photocatalyst for decomposing organic compounds due to its strong photocatalytic activity, chemical and biological inertness and high photochemical stability. Extensive literature analysis has shown many possibilities to improve the efficiency of photodecomposition of organic compounds over TiO_2. Clay minerals with large surface areas for adsorption and high adsorption capacity used to synthesize nanocomposites with TiO_2 (especially anatase) enhance the decomposition of organic pollutants by photocatalytic degradation. Recently, clay minerals have been used more often to prepare hybrid photocatalysts. Dispersing TiO_2 nanoparticles onto the surfaces of clay minerals improves the photocatalytic activity of TiO_2 by providing more active surface sites and reducing the agglomeration of TiO_2 particles. The present review paper offers the following: an overview of the trend in the use of the clay/TiO_2 nanocomposite photocatalysts, especially halloysite/TiO_2 materials for removal of organic contaminants from water, report on the recent work done and important applications for photocatalytic degradation of organic pollutants.

1. Introduction

Among the advanced oxidation processes for water purification, heterogeneous photocatalysis is an efficient, economical and environmentally friendly technology of removing organic impurities (Guillard et al., 1999; Houas et al., 2001; Konstantinou and Albanis, 2003, 2004). During that process, the semi-conductor illuminated by the light of the proper wavelength generates active species, which oxidize organic compounds dissolved in water. Among semiconductor photocatalysts (TiO_2, ZnO, Fe_2O_3, CdS, etc.), TiO_2 has become a photocatalyst in environmental decontamination for a large variety of organics, viruses, bacteria, fungi, algae and cancer cells, which can be totally degraded and mineralized to CO_2, H_2O and harmless inorganic anions. Titanium dioxide (with sizes ranging from clusters and colloids to powders and large single crystals) is one of the most popular and promising material for decomposing organic compounds due to its strong photocatalytic property, chemical and biological inertness, high photochemical stability and low price (Fujishima et al., 2000; Carp et al., 2004; Stylidi et al., 2004; An et al., 2010; Muneer et al., 2010; Zhang et al., 2011a,b). It is well known that TiO_2 powders, especially in the form of anatase, have good catalytic activities because of their large specific surface area where reactions take place (Zhao et al., 2006), but the combination with a small fraction of rutile has also shown excellent photocatalytic activities (e.g. Degussa-P25) (Ohno et al., 2001).

Photocatalysis based on TiO_2 (anatase) has the following advantages (Carp et al., 2004):

- a non-selective destruction of organic and inorganic waste materials achieved under ambient temperature and pressure without production of polycyclic products;
- oxidation of pollutant in ppb range;
- the use of oxygen as the oxidant;
- capability for simultaneous oxidative and reductive reactions;
- in particular, photocatalysis is known to be effective for inactive substances, which opens perspectives in oil spill cleaning, elimination of surfactants and dyes from industrial water;
- these highly active catalysts can be adaptable to specially-designed reactor systems.

The fundamentals of photocatalysis consist in hitting the semiconductor with radiation of energy near to, or greater than its band gap energy, generating high energy electron–hole pairs, which initiate the heterogeneous photocatalytic reaction. However, low efficiency under irradiation in the visible region (limited photoresponse range (<380 nm)), small specific surface area and low adsorption ability are the main drawbacks associated with the use of non-modified TiO_2, which hinder its application (Asahi et al., 2001; Zhang et al., 2008a,b). To overcome these limitations, numerous strategies have been adopted, including doping with various transition metal ions, metal coating, surface sensitization and semiconductor coupling (Li and Li, 2002; Hu et al., 2003a,b; Sivalingam et al., 2003; Arana et al., 2004; Carp et al., 2004;

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Chiang et al., 2004; Coleman et al., 2005; Li et al., 2005; Chen and Mao, 2007; Tong et al., 2007; Egerton and Mattinson, 2008; Li et al., 2008a; Liu et al., 2008; Young et al., 2008; Wodka et al., 2010).

Heterogeneous photocatalytic reactions occur on the photocatalyst surface and pre-adsorption of target compounds is necessary for their degradation. This is achieved by using supports with large surface areas for adsorption and high adsorption capacity for target substances. Adsorption strength should be moderate enough to allow the diffusion of adsorbed substrates to the loaded TiO_2 (Xu and Langford, 1997). As support materials, activated carbon (Takeda et al., 1998; Nozawa et al., 2001), stainless steel (Zhu et al., 2001), silica (Xu et al., 1999; Chun et al., 2001; Ding et al., 2001; Aguado et al., 2002; Tanaka et al., 2002; Hu et al., 2003a,b; Vohra and Tanaka, 2003), zeolites (Xu and Langford, 1997; Durgakumari et al., 2002; Reddy et al., 2003), or clay minerals (Kaneko et al., 2001; Mogyorósi et al., 2002; Sun et al., 2002; Ooka et al., 2003; Kun et al., 2006; Kibanova et al., 2009; Papoulis et al., 2010, 2013a,b) were used to prepare hybrid photocatalysts. Recently, much attention has been paid to clay minerals used as supports of TiO_2-based photocatalysts. Dispersing TiO_2 nanoparticles onto the surfaces of clay minerals improves the photocatalytic activity by providing more active surface sites (Mogyorósi et al., 2002; Kibanova et al., 2009; Papoulis et al., 2010; Papoulis et al., 2013a,b). Clay minerals used to synthesize nanocomposites of TiO_2 (especially anatase) can reduce anatase agglomeration and enhance the decomposition of organic and inorganic pollutants by photocatalytic degradation (Mogyorósi et al., 2002; Kibanova et al., 2009; Papoulis et al., 2010, 2013a,b).

The main focus of this review is directed to research advances of the past decade concerning clay/TiO_2 nanocomposites, especially halloysite/TiO_2 materials. This review compares the data on the synthesis method and the applications of clay/titania composites. A literature review was made and selected experimental approaches were summarized with an emphasis on photocatalytic degradation of organic pollutants.

2. Mechanism of TiO_2-assisted photocatalytic degradation

The mechanism of TiO_2-assisted photocatalysis has already been reported in detail in the literature (Zhan and Tian, 1998; Bandara et al., 1999; Fujishima et al., 2000; Tanaka et al., 2000; Bianco-Prevot et al., 2001; Galindo et al., 2001; Houas et al., 2001; Daneshvar et al., 2003). Photocatalytic reaction is initiated when an aqueous dispersion of TiO_2 is illuminated with light energy greater than its band gap energy (e.g., 3.2 eV) and conduction band electrons (e^-) are generated. Consequently, valence band holes (h^+) are generated (Eq. (1)). The photogenerated holes can react with OH^- or H_2O oxidizing them into OH• radicals (Eqs. (2)–(3)). Since oxygen is an easily reducible substance, the reduction of oxygen adsorbed on the Ti(III)-surface or dissolved in water by the photoelectron of the conduction band results in generating superoxide radical anions ($O^{2}•^{-}$), which in turn react with H^+ to generate hydrogen dioxide radical (•HO_2, hydroperoxyl) (Eqs. (5)–(7)). During subsequent collisions with an electron a hydrogendioxide(1-) anion (HO_2^-, hydrogenperoxide(1)) is produced and H_2O_2 is eventually formed (Eqs. (7)–(11)).

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \quad (1)$$

Reaction involving valence band h^+

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + {}^{\bullet}OH + H^+ \quad (2)$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + {}^{\bullet}OH \quad (3)$$

$$TiO_2(h^+) + 2H_2O \rightarrow TiO_2 + H_2O_2 + 2H^+ \quad (4)$$

Reaction involving conduction band e^-

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \quad (5)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \quad (6)$$

$$TiO_2(e^-) + HO_2^{\bullet} \rightarrow TiO_2 + HO_2^- \quad (7)$$

$$TiO_2(e^-) + O_2^{\bullet} + 2H^+ \rightarrow TiO_2 + H_2O_2 \quad (8)$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^- \quad (9)$$

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

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (11)$$

Photoholes have great potential to oxidize organic species directly or indirectly via the combination with •OH predominant in aqueous solutions (Eqs. (12) and (13)) (Fujishima et al., 2000).

$$R\text{-}H + {}^{\bullet}OH \rightarrow R'^{\bullet} + H_2O \quad (12)$$

$$R\text{-}H + h^+ \rightarrow R^{+\bullet} \rightarrow \text{Degradation products} \quad (13)$$

Hydroxyl radicals (•OH), holes (h^+), superoxide ions ($O^{2}•^{-}$) and peroxide radicals (•HO_2) are highly reactive intermediates that will oxidize a large variety of organic compounds (Kumar and Mathur, 2004; Canle et al., 2005; Karunakaran et al., 2005).

Photooxidative degradation of many organic pollutants over titania has been extensively reviewed (Konstantinou and Albanis, 2004; Gaya and Abdullah, 2008). Both the mechanism of decomposition and the number of intermediates depend upon the nature of organic compounds. The degradation of phenol, aniline and its derivatives has been widely studied (Sanchez et al., 1997; Di Paola et al., 2003; Canle et al., 2005; Guo et al., 2006; Chu et al., 2007; Silva et al., 2009), because these compounds are important chemical wastes, showing toxicity, great persistence and low natural biodegradability. During the photochemical degradation of phenol with TiO_2 the OH• radical attacks the phenyl ring of the phenol molecule, yielding several intermediates (Guo et al., 2006): catechol (b), resorcinol (c), benzene-1,2,3-triol(d) and hydroquinone (e), then the phenyl rings in these compounds break up to give maleic acid (f), then short-chain organic acids such as, 3-hydroxy propyl carboxylic acid (g), 2-hydroxy propanal (i), 2-hydroxy-ethanoic acid glycol acid (j), finally CO_2 and H_2O (Fig. 1).

The photocatalytic degradation of 2-, 3- and 4-nitrophenol in oxygenated aqueous dispersions containing TiO_2 leads to complete mineralisation of the substrates (Carp et al., 2004; Di Paola et al., 2003). The formation of dihydroxynitrobenzene isomers confirms that the hydroxyl radical oxidation is the major reaction pathway in the photocatalytic degradation of the three isomeric nitrophenols. Nitrite ions are formed in the early stages of the process, whereas nitrate and ammonium ions are present at the end of the degradation (Fig. 2).

As intermediate products resulting from the photodegradation of aniline, some hydroxylated aromatic compounds such as phenol, 2-aminophenol, hydroxyhydroquinone, paraquinone and nitrobenzene were formed (Sanchez et al., 1997; Carp et al., 2004; Canle et al., 2005). The formation of these intermediates confirmed the •OH radical mediated mechanism of aniline photodegradation (Fig. 2).

3. Photocatalytic activity of clay/TiO_2 nanocomposites

The use of titania nanopowders in solution causes some practical problems, such as photocatalyst agglomeration and difficult recovery. Additionally, despite the fact that TiO_2 is referred to as a material with very low toxicity (Warheit et al., 2007; Chawengkijwanich and Hayata, 2008), the possible risk of applying TiO_2 photocatalyst was