Applied Catalysis B: Environmental 203 (2017) 247–269

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Review

Photocatalytic oxidation technology for indoor environment air purification: The state-of-the-art

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ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form 10 October 2016
Accepted 13 October 2016
Available online 17 October 2016

Keywords:
Photocatalytic oxidation
Titanium dioxide (TiO_2)
Air purification
Volatile organic compounds (VOCs)
Reaction intermediates

ABSTRACT

Inevitable presence of volatile organic compounds (VOCs) in indoor environment and their adverse impact on human health and productivity have encouraged the development of various technologies for air pollution remediation. Among these technologies, photocatalytic oxidation (PCO) is regarded as one of the most promising methods and has been the focus of many research works in the last two decades. Titanium dioxide (TiO_2) is by far the most investigated photocatalyst for photocatalytic degradation of gaseous VOCs. This review article is intended to provide a comprehensive overview of the application of commercial TiO_2 photocatalysts for removal of VOCs in air. First, the fundamentals of photocatalytic oxidation are briefly discussed and common TiO_2-based photocatalysts are introduced. Then, the relations between the characteristics of photocatalysts (e.g. crystallinity, surface area and surface chemistry) and photocatalytic activity as well as the influence of key operating parameters on PCO processes are investigated. Afterwards, the reaction mechanisms and identified reaction intermediates/by-products for the most prevalent VOC families are reviewed. Finally, the paper discusses the deactivation of photocatalysts during PCO processes and some of the common regeneration techniques.

Contents

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http://dx.doi.org/10.1016/j.apcatb.2016.10.037
0926-3373/

1. Introduction

Owing to the fact that nowadays people spend most of their time (more than 90% [1]) in an indoor environment, indoor air quality (IAQ) has a significant impact on human health, comfort and productivity [2]. A long-term exposure to indoor air pollutants can be detrimental to human health and lead to sick building syndrome, building related illnesses and in extreme cases cancer [3]. VOCs, nitrogen oxides (NO_x), carbon monoxide (CO), and particulate matter are among the main indoor air pollutants. Levels of pollutants in indoor environment can be higher than that of outdoor air due to the contribution of indoor sources such as combustion by-products, building materials, office equipment (e.g. printers and computers), and consumer products [3,4]. VOCs mainly contain alkanes, aromatics, esters, alkenes, carboxylic acids and alcohols [2]. Considering the growing concerns regarding the IAQ, many technologies have been developed for removing VOCs from indoor air such as adsorption [5–8], ozonation [9–11], non-thermal plasma [12,13], and photocatalytic oxidation [14–17].

In the last two decades, PCO technology has attracted great attention for removal of gaseous pollutants at low concentrations (i.e. part per billion (ppb) level), owed to its superior features such as room temperature operation, activity towards various contaminants, and benign final products (CO_2 and H_2O). PCO technology is basically founded on the application of semiconductor catalysts, such as TiO_2, and ultraviolet (UV) light to convert challenge compounds into less harmful products. In PCO, a crucial step is the formation of electron and hole (e^--h^+) pairs which requires the illumination of semiconductor, absorption of photons with sufficient energy, and promotion of electrons from the valence band to the conduction band [18]. The photogenerated charge carriers participate in a series of reactions with other molecules such as oxygen and water and produce highly reactive radicals (such as hydroxyl radical). In gas phase PCO, mass transfer of the VOC compounds from the gas phase (i.e. air stream) to the solid phase plays an important role and greatly affects the reaction rate and removal efficiency. After the external (from bulk to exterior surface) and internal diffusions (from exterior surface to internal catalytic surface) and adsorption onto the surface, pollutant molecules come into contact with the produced reactive species and break down to lower molecular weight products and eventually to CO_2, water and other by-products [2,19]. The basic PCO reaction mechanism using TiO_2 can be depicted as follows:

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (1)$$

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

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

$$TiO_2(e^+_{CB}) + O_2 \rightarrow TiO_2 + O^\bullet{}^-_2 \quad (4)$$

$$O^\bullet{}^-_2 + H^+ \rightarrow H^\bullet{}_2 \quad (5)$$

$$HO^\bullet{}_2 + HO^\bullet{}_2 \rightarrow H_2O_2 + O_2 \quad (6)$$

$$TiO_2\left(e^-_{CB}\right) + H_2O_2 \rightarrow OH^- + OH^\bullet \quad (7)$$

$$VOC + O_2 + OH^\bullet \rightarrow H_2O + CO_2 + other\ products \quad (8)$$

Apart from their beneficial participation in oxidation and reduction reactions, electrons and holes also go through recombination process where they neutralize one another. The recombination of charge carriers, whether in the bulk or on the surface, drastically decreases the quantum efficiency and accordingly the PCO performance [20].

Among a wide spectrum of photocatalysts (e.g. TiO_2, ZnO, ZrO_2, SnO_2, WO_3, CeO_2, ZnS, and Fe_2O_3), TiO_2, as the most promising photocatalyst, has been the focus of majority of the works owing to its moderate performance as a photocatalyst under UV light irradiation, chemical stability, and suitable positions of valence and conduction bands [21]. To date, numerous TiO_2 photocatalysts with different morphological designs have been developed: nanoparticles, nanotubes, hollow fibers, and mesoporous [4,22]. As one can note by the number of publications in the past 15 years, there is great interest in the application of commercial photocatalysts for the removal of VOCs from air. To this end, extensive research efforts have been devoted to evaluate the performance of several commercially available photocatalysts for such application. TiO_2 Aeroxide P25 from Evonik® is by far the most employed photocatalyst in this field owing to its high performance in degradation of many VOCs, availability, and relatively low cost [23]. The other common commercial titanium dioxides are PC series (Cristal Global Companies), Hombicat® UV100, and Aerolyst 7710 (Evonik®) [24–27]. Table 1 summarizes some of the key characteristics of different commercial photocatalysts.

In most of the published articles, limited explanations were provided to enable the reader make connections between the morphology, electronic properties, and surface chemistry of the photocatalyst and the obtained photocatalytic activity toward a specific VOC. It is believed that a comprehensive review of TiO_2 photocatalysts, specifically applied in the PCO of indoor air pollutants, would provide more insight into the crucial characteristics needed in an efficient and long-lasting photocatalyst.

2. Photocatalyst characteristics

Photocatalytic performance of TiO_2 depends on several factors including crystallinity, crystalline phase, crystal size, accessible surface area, pore structure, pore size, and adsorption capacity [33,34]. Depending on the target VOC and the main operating parameters, the abovementioned properties can affect the photocatalytic activity to different extents.

2.1. Effect of photocatalyst crystallinity and crystal size

Light harvesting, charge carrier generation (i.e. electron excitation) and separation, and charge migration to the surface exert significant influence on the quantum efficiency and photocatalytic activity of TiO_2. Due to the fact that recombination process is facilitated by the presence of lattice defects, crystal imperfections and impurities, much attention has been paid to the achievement of high bulk crystallinity in order to enhance the photon utilization efficiency [35]. Anatase and rutile are the main crystalline structures of TiO_2 with energy band-gaps of 3.23 and 3.02 eV, respectively [36]. It is generally recognized that anatase is more active than rutile, which can be ascribed to several properties of anatase phase: (i) better generation of e^--h^+ pair; (ii) higher affinity towards O_2 due to the more negative redox potential of conduction band; (iii) higher amount of surface hydroxyl groups which improve chemisorption properties; and (iv) lower recombination rate than rutile [4,33].

In the case of P25, it seems that the source of its high photocatalytic activity is still a matter of debate [23]. It has been suggested that due to the co-presence of anatase and rutile phases, e^--h^+ can transfer between interconnecting anatase and rutile particles and prevent charge recombination [37,38]. Ohno et al. [39] attributed the high photocatalytic activity of P25 to the band bending in rutile particles which are in contact with anatase particles. On the other hand, Bickley et al. [40] proposed that the key reason for P25 high activity is the presence of particles made of anatase nuclei inside a rutile layer which elongates the e^--h^+ lifetime (e^- in anatase and h^+ in rutile). Some studies have employed time resolved microwave conductivity (TRMC) to study the charge carrier trans-