Review

Photocatalytic purification of volatile organic compounds in indoor air: A literature review

Jinhan Mo [a], Yinping Zhang [a,*], Qiujian Xu [a], Jennifer Joaquin Lamson [a,b], Rongyi Zhao [a]

[a] Department of Building Science, Tsinghua University, Beijing 100084, PR China
[b] Department of Energy and Environment Engineering, Oslo University College, Norway

ARTICLE INFO

ABSTRACT

Volatile organic compounds (VOCs) are prevalent components of indoor air pollution. Among the approaches to remove VOCs from indoor air, photocatalytic oxidation (PCO) is regarded as a promising method. This paper is a review of the status of research on PCO purification of VOCs in indoor air. The review and discussion concentrate on the preparation and coating of various photocatalytic catalysts; different kinetic experiments and models; novel methods for measuring kinetic parameters; reaction pathways; intermediates generated by PCO; and an overview of various PCO reactors and their models described in the literature. Some recommendations are made for future work to evaluate the performance of photocatalytic catalysts, to reduce the generation of harmful intermediates and to design new PCO reactors with integrated UV source and reaction surface.

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1. Introduction

Indoor air pollutants impact human health, comfort and productivity. Volatile organic compounds (VOCs) are among the most abundant chemical pollutants in the indoor air that we breathe (WHO, 1989; USEPA, 1990). Some of these compounds are associated with sick building syndrome (SBS) including mucous membrane irritation, headache and fatigue (WHO, 1989; USEPA, 1990; Little et al., 1994; Meininghaus et al., 1999; Kim et al., 2001; Wang et al., 2007; Auvinen and Wirtanen, 2008); others are known carcinogens (e.g., formaldehyde, acrolein (OEHHA, 2007)). Millions of people are currently suffering from the consequences of poor indoor air quality and billons of dollars are lost in the world each year due to poor indoor air quality (Fisk and Rosenfeld, 1997). Many advanced technologies for the quick and economical removal of VOCs from indoor air have recently been developed. Among these, photocatalytic oxidation (PCO) is an innovative and promising approach (Tompkins, 2001).

As the pioneers in this field, Fujishima and Honda (1972) discovered the phenomenon of photoinduced water cleavage to TiO$_2$ electrodes. In the subsequent three decades, a wide range of potential applications of PCO to air purification have been reported.

A literature search using the ISI Web of Knowledge database of articles published prior to March 2008 was carried out. The search keywords used were "photocatalytic oxidation" and "air or gas". The literature search identified 1906 articles. Of these, 1264 articles were excluded for one or more of the following reasons: (i) the studies performed were not on indoor air; (ii) they lacked data on VOCs, (iii) they were written in a language other than English. Consequently, 168 studies have been scrutinized for this paper.

The air purification technique of PCO commonly uses nano-semiconductor catalysts and ultraviolet (UV) light to convert organic compounds in indoor air into benign and odorless constituents – water vapor (H$_2$O) and carbon dioxide (CO$_2$) (Tompkins, 2001). Most PCO reactors use nano-titania (TiO$_2$) as the catalyst that is activated by UV light. Fig. 1 shows the schematic of the UV-PCO process of VOCs using TiO$_2$ as the catalyst. An electron in an electron-filled valence band (VB) is excited by photo-irradiation to a vacant conduction band (CB), leaving a positive hole in the VB. These electrons and positive holes drive reduction and oxidation, respectively, of compounds adsorbed on the surface of a photocatalyst (Ohtani, 2008).

The activation equation can be written as:

$$TiO_2 + hv \rightarrow h^+ + e^- \qquad (1)$$

In this reaction, h$^+$ and e$^-$ are powerful oxidizing and reducing agents, respectively. The oxidation and reduction reactions can be expressed as:

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* Corresponding author. Fax: +86 10 6277 3461.
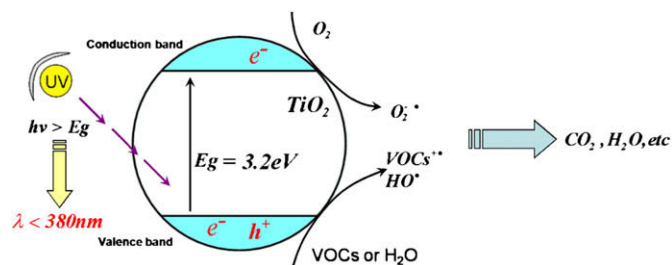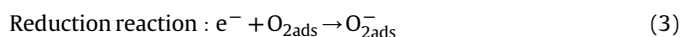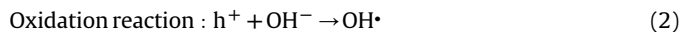 E-mail address: zhangyp@tsinghua.edu.cn (Y. Zhang).

Fig. 1. Schematic of TiO$_2$ UV photocatalytic oxidation process of VOCs.

$$\text{Oxidation reaction}: \mathrm{h}^+ + \mathrm{OH}^- \rightarrow \mathrm{OH}\cdot \qquad (2)$$

$$\text{Reduction reaction}: \mathrm{e}^- + \mathrm{O}_{2\mathrm{ads}} \rightarrow \mathrm{O}_{2\mathrm{ads}}^- \qquad (3)$$

When organic compounds are chemically transformed by a PCO device, it is the hydroxyl radical (OH•), derived from the oxidation of adsorbed water or adsorbed OH$^-$, that is the dominant strong oxidant. Its net reaction with a VOC can be expressed as:

$$\mathrm{OH}\cdot + \mathrm{VOC} + \mathrm{O}_2 \rightarrow n\mathrm{CO}_2 + m\mathrm{H}_2\mathrm{O} \qquad (4)$$

The process of PCO has several advantages (Ollis, 2000): (1) GRAS (Generally Recognized As Safe): the common photocatalyst is anatase TiO$_2$, an n-type semiconductor oxide which is also a component of some toothpastes and pharmaceutical suspensions; (2) Mild oxidant: Kinetic studies demonstrate that the ultimate source of oxygen during oxidation is molecular oxygen, a far milder oxidant than hydrogen peroxide or ozone, etc.; (3) Ambient temperature: photocatalysis appears to be active at room temperature; (4) general: while several mechanistic pathways for oxidation have been proposed, the dominant view is that the hydroxyl radical (or some other equally strong oxidant) is photogenerated on the titania surface; the potency of this oxidant is responsible for the titania's broad activity toward various contaminants (such as aromatics, alkanes, olefins, halogenated hydrocarbons, odor compounds etc.).

This paper is intended to provide a comprehensive review of the current understanding of PCO for indoor air purification, including photocatalysts, experiments, photocatalytic reactors, as well as the intermediates (see Fig. 2). This will be followed by a discussion of the kinetic models of the PCO process. Subsequently, the mechanism models of PCO reactors and the enhancement methods of PCO reactor performance are reviewed. The identification of PCO intermediates or by-products is summarized and discussed in the final section of this paper.
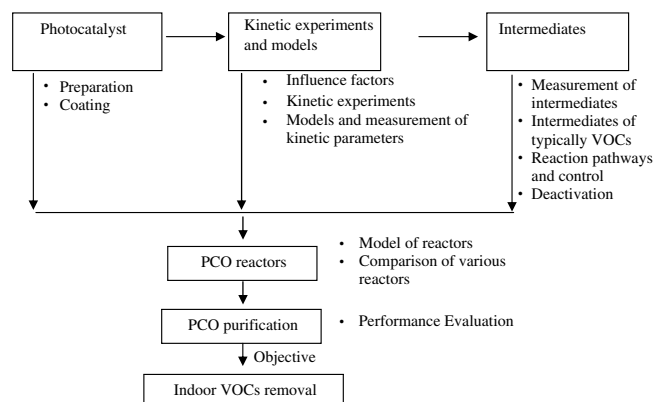

Fig. 2. Review frame of PCO.

2. Photocatalysts

Various catalysts have been developed for PCO applications. Table 1 summaries some of the photocatalysts described in the literature.

2.1. Common photocatalysts

The common photocatalysts are primarily metal oxides or sulphides, i.e., TiO$_2$, ZnO, ZrO$_2$, SnO$_2$, WO$_3$, CeO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, ZnS and CdS (Hoffmann et al., 1995). The most popular choices of photocatalysts are TiO$_2$ and ZnO. Teichner et al. (Ollis, 2000) explored the photoactivity of numerous oxides for hydrocarbon partial oxidation in the gas phase, finding that the active catalysts involving titania, zinc, and tungsten ranked in the activity sequence: TiO$_2$ (anatase) > ZnO > WO$_3$. Much of the published work on photocatalysis uses TiO$_2$ as it is relatively inexpensive, stable chemically, and the photogenerated holes are highly oxidizing (Fujishima and Zhang, 2006). TiO$_2$ has two crystal forms: anatase and rutile. The energy band-gaps of anatase and rutile are 3.23 and 3.02 eV, respectively. The commercial Degussa P25 prepared by flame pyrolysis (Maira et al., 2000) was used widely in air purification (Larson et al., 1995; Kirchnerova et al., 2005) with a primary particle diameter of 300 nm, a surface area of 50 m^2 g^{-1}, and a crystal distribution of 70% anatase and 30% rutile (Larson et al., 1995). In addition, many researchers have attempted to improve the catalytic activity of photocatalysts by synthesizing semiconductor metal nanoparticle composites and to extend the photoresponse into the visible range by doping metal ions into TiO$_2$ (Ollis, 2000).

2.1.1. Visible light responsive photocatalyst

Usually, there are three ways to prepare the visible light responsive photocatalyst: doping TiO$_2$ with transition metal ions; doping nitrogen into TiO$_2$ and utilizing sensitizing dyes (Kamat and Meisel, 2002).

Coupling of TiO$_2$ with a small band-gap semiconductor or doping with transition metal ions such as V, Cr, Mn, Fe, Co, Ni, or Cu extends light absorption into the visible region (Zang et al., 2000). The coupling of low concentrations of WO$_3$ (4 wt.%) with mesoporous anatase TiO$_2$ led to high photocatalytic efficiency using both UV and visible light activation on toluene decomposition (Bosc et al., 2006). Furthermore, even though metal ion doping extended the response into visible light, the photocatalytic performance in the UV region decreased significantly (Kamat and Meisel, 2002). Brezova et al. (1997) found the presence of metals, such as Li$^+$, Zn^{2+}, Cd^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Al^{3+}, Mn^{2+} and Pt$^\circ$, may significantly change the photoactivity of TiO$_2$. He used the sol–gel technique to prepare the M^{n+}/TiO$_2$ layers for phenol degradation (M^{n+} ≡ Li$^+$, Zn^{2+}, Cd^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Al^{3+}, Mn^{2+} and Pt^0). It was indicated that the presence of Co^{3+}, Cr^{3+}, Ce^{3+}, Mn^{2+}, Al^{3+} and Fe^{3+} ions in the TiO$_2$ photocatalyst (5 mol% M^{n+}:Ti^{4+}) has a detrimental effect on its photoactivity. A study of Uosaki et al. (Kamat and Meisel, 2002) has shown that inclusion of transition metal ions decreased photocatalytic activity of TiO$_2$ under UV irradiation. The metal ions act as recombination sites for the photogenerated charge carriers.

Various nitrogen-doped TiO$_2$ were found to photodegrade gaseous formaldehyde (Irokawa et al., 2006), acetaldehyde (Asahi et al., 2001; Irokawa et al., 2006), acetone (Ihara et al., 2003), 2-propanol (Irie et al., 2003; Miyauchi et al., 2004) and toluene (Irokawa et al., 2006; Wu et al., 2008). TiO$_{2-x}$N$_x$ (films and powders) has better photoactivity than TiO$_2$ under visible light irradiation. The active wavelength of TiO$_{2-x}$N$_x$, of less than 500 nm, covers the main peak of the solar irradiation energy beyond Earth's atmosphere (around 460 nm) (Asahi et al., 2001). Additional introduction of ZrO$_2$ into TiO$_{2-x}$N$_x$ displayed higher porosity, higher specific surface area, and an improved thermal stability than the