

Photocatalytic degradation of volatile pollutants

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ABSTRACT

Photocatalytic oxidation is a promising technology for the removal of gas-phase volatile organic compounds. This technique is cost-efficient, simple to perform, yields high removal of the pollutants and does not generate large

quantities of waste. In this mini-review, the application of photocatalytic oxidation for waste-gas treatment, the mechanisms involved and the operational aspects to be considered for enhanced reactor performance has been reviewed in brief.

Key Words: Photocatalyst; photoreactor; waste-gas; volatile organic compounds; elimination capacity.

The Volatile Organic Compounds (VOCs) are an important class of air pollutant that is of health and environmental concern. The United States Environmental Protection Agency has stipulated clear guidelines on the toxic threshold levels of different VOCs and also recommended stringent guidelines for polluting industries. From a pollution control view point, a wide variety of VOCs can be mineralized to innocuous end-products using a photocatalyst such as TiO₂ [1,2]. Gas-phase heterogeneous photocatalysis using TiO₂ was first explored by Dibble et al. [3]. In those previous works, the authors reported high levels Trichloroethylene (TCE) destruction, i.e. removal. Since then, extensive research pertaining to the photodegradation of volatile aldehydes, ketones, alcohols, aromatics and chlorinated compounds have been carried out by different researchers [4-11].

The principle of Photocatalytic Oxidation (PCO) depends on the use of a semi-conductor such as TiO₂ and Ultraviolet (UV) light to transform VOCs into less harmful (innocuous) products [1]. The vital step in PCO is the separation of two types of carriers: an electron (e⁻) and a hole (h⁺) which requires the illumination of the TiO₂ surface and absorption of photons with sufficient energy to promote an electron from the valence band (VB) to the Conduction Band (CB) [1,7]. The hydroxyl radical (OH•) is produced during photocatalysis which acts as a powerful redox transient species in photocatalysis. As the most powerful oxidizing agent, it is mainly responsible for being able to attack the VOCs, i.e. to degrade the pollutants [7]. The photocatalytic oxidation of volatile pollutants to end-products and the basic PCO reaction mechanisms are shown in Figure 1 and Table 1, respectively.

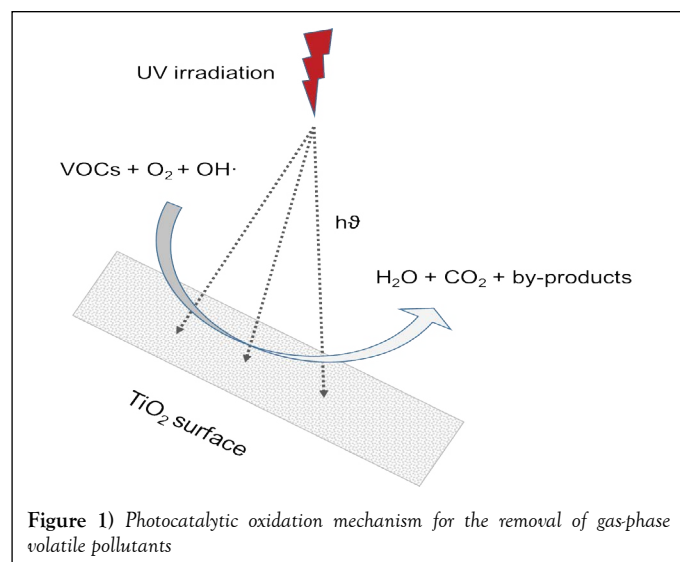


Figure 1) Photocatalytic oxidation mechanism for the removal of gas-phase volatile pollutants

Table 1

Fundamental reaction mechanisms of TiO₂ photocatalyst for the removal of VOCs [1]

Reactions
$TiO_2 + h\nu \rightarrow TiO_2 (e_{CB}^- + h_{VB}^+)$
$TiO_2 (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^{\bullet}OH$
$TiO_2 (h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^{\bullet}$
$TiO_2 (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -}$
$O_2^{\bullet -} + H^+ \rightarrow H_2O_2$
$H_2O_2 + HO_2^{\bullet} \rightarrow H_2O + O_2$
$TiO_2 (e_{CB}^-) + H_2O_2 \rightarrow OH^{\bullet} + OH^-$
$VOC + O_2 + OH^{\bullet} \rightarrow H_2O + CO_2 + \text{other products}$

High chemical stability, high oxidizing capability, non-toxicity and low cost are the main advantages of applying TiO₂ in a wide range of environmental engineering applications [1,2]. Anatase, brookite and rutile are the three existing crystalline modifications of TiO₂ [7]. There are several TiO₂ photocatalysts having different morphological designs such as nanoparticles, hollow fibres, nanotubes and mesoporous structures. Several factors such as the crystallinity, crystal size, crystalline phase, accessible surface area, pore size, pore structure and adsorption capacity determine the performance of TiO₂. Besides, There are some promising technologies for modifying TiO₂ photocatalytic efficiency, i.e. metal doping (doped with metal like Fe, Cu, Ni, V, Pt, Pd, Ag, Ru, Co and Mn), non-metal doping (doped with non-metal like B, C, N and S) and co-doping (e.g. doped with B and Fe) which can enhance the photocatalytic activity through increasing the charge separation and shifting 'the light absorption range towards visible light'. Various commercial TiO₂ based photocatalysts (e.g. Hombicat® UV100, Aeroxide P25 and Aerolyst 7710 from Evonik®) are available for the removal of VOCs. The photocatalytic conversion of VOCs can be in the range of 30-100% depending on several factors: type of support materials, type of VOCs, VOC concentration and composition, the oxidation/reaction pathways, residence time, relative humidity and light intensity [1,2].

Two typical examples where PCO can be applied are the petrochemical industry and the pharmaceutical industry. These two industries produce waste-gas that contain high concentrations of aromatic hydrocarbons, aliphatics, amines and other trace organics. The composition and concentration of the waste-gas often vary, i.e. with operational time of the day, depending on the production/manufacturing schedule of the process industry, the raw materials used, the end-products produced and the efficiency of the process unit. The performance of photocatalytic reactors will depend on the pollutant characteristics such as solubility, adsorptivity, bond structure, potential degradability and operating conditions. Furthermore, competitive effects such as pollutant-pollutant interactions, pollutant-photocatalyst interaction, pollutant-intermediate interaction and abiotic factors can also play an important role in determining the mass transfer characteristics and the

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Table 2:
Recent experimental modifications on the photocatalytic degradation of VOCs

Photocatalyst	Analytical technique	Pollutants	Inlet pollutant concentration	Residence time, s	Removal efficiency, %	Remarks	References
Commercial TiO ₂ : P25, PC 500, S5-300A and UV100	GC-MS HPLC	Toluene	~ 1000 ppb	0.02 0.05 0.1	~ 20-60 ~ 30-75 ~ 45-80	By-products generation: Formaldehyde (< 15 ppb) Acetaldehyde (< 8 ppb) Acetone (< 10 ppb)	[21]
		MEK	~ 1000 ppb	0.02 0.05 0.1	~ 25-55 ~ 35-60 ~ 48-65	Formaldehyde (> 40 ppb) Acetaldehyde (> 40 ppb) Acetone (< 20 ppb)	
Commercial TiO ₂ : nanometric, P25 (Evonic) and micrometric, 1077 (kronos)	PTR-MS	17 VOCs in mixture:					
		Aldehydes	~ 5-40 ppb	~ 1200	69-74	'VOCs compete for the adsorption on the catalyst surface'	[22]
		Hydrocarbons	~ 12-40 ppb	~ 1200	72-86		
Chlorinated compounds	~ 5-22 ppb	~ 1800	82-84				
Fabricated mesoporous TiO ₂ (calcined at 400°C)	VUV-PCO process GC O ₃ analyser	Benzene	25 ppmv			Calcination temperature significantly affects the catalytic activity and structural properties of TiO ₂	[18]
		Under UV radiation VUV radiation					
TiO ₂ nanotubes	Photoacoustic gas monitor	Acetaldehyde	50 ppmv	~ 1800	~ 99	Doubly open-ended TiO ₂ nanotubes favours photocatalytic activity	[19]
		Toluene	20 ppmv	~ 1800	~ 90		

photo (catalytic) degradation steps. In some instances, however, depending on the nature of the parent VOC, the production rate of the intermediates may be higher than the removal rate of the pollutant itself. This could cause malfunctioning of the reactor setup, leading to transient-type behaviours and a reduction in the elimination capacity/removal efficiency [12,13].

According to Kovalevskiy et al. [14], adsorption of pollutants on the surface of the photocatalyst is an important step that determines the success of every PCO process. Thus, it is recommended to choose a photocatalyst that offers high surface area and that has high moisture retention capacity to facilitate the PCO reaction. It is also recommended to increase the photocatalytic performance by increasing the surface area of the catalyst which can be done by immobilizing the photocatalyst (e.g. TiO₂) on porous supports [15]. Besides, the hydrophobic or hydrophilic properties of the pollutant, the functional groups on the photocatalyst and also the ability of the intermediates formed to adhere to the surface of the photocatalyst should be carefully considered [16,17].

Catalytic deactivation, e.g. blockage of the active sites, fouling and aggregation of the photocatalyst (TiO₂), dehydroxylation of TiO₂ surface, generation of by products and inefficiency are the main limitations of the PCO process. However, there are various approaches to regenerate the photocatalyst by just passing dry air under UV light for a long period of time, high temperature calcination, ozone-purging in the presence of humidity, etc, among others. The photocatalytic activity can also be enhanced by using any one of the following strategies: vacuum based UV treatment, VUV irradiation instead of UV irradiation, activated carbon or porous silica to provide superior porous support, and the use of doubly open-ended structure of TiO₂ nanotubes [1,15,18,19]. The recent literature reports (only representative) on the application of PCO for waste-gas treatment are shown in Table 2. As evident from these studies, most of the research on PCO have been carried out under ideal, laboratory conditions [20-23]. Hence, for future studies, several important concerns should be considered: (i) understand the hydrodynamics of the PCO reactor under multi-phase flow conditions, (ii) flow visualization tests, (iii) ascertain the rate-limiting step of the PCO process, (iv) development of novel photocatalyst, and (v) process scale-up and cost-benefit analysis.

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