

Review

Recent Developments in Photocatalytic Nanotechnology for Purifying Air Polluted with Volatile Organic Compounds: Effect of Operating Parameters and Catalyst Deactivation

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Abstract: Photocatalytic oxidation (PCO) is a successful method for indoor air purification, especially for removing low-concentration pollutants. Volatile organic compounds (VOCs) form a class of organic pollutants that are released into the atmosphere by consumer goods or via human activities. Once they enter the atmosphere, some might combine with other gases to create new air pollutants, which can have a detrimental effect on the health of living beings. This review focuses on current developments in the degradation of indoor pollutants, with an emphasis on two aspects of PCO: (i) influence of environmental (external) conditions; and (ii) catalyst deactivation and possible solutions. TiO₂ is widely used as a photocatalyst in PCO because of its unique properties. Here, the potential effects of the operating parameters, such as the nature of the reactant, catalyst support, light intensity, and relative humidity, are extensively investigated. Then the developments and limitations of the PCO technique are highlighted, especially photocatalyst deactivation. Furthermore, the nature and deactivation mechanisms of photocatalysts are discussed, with possible solutions for reducing catalyst deactivation. Finally, the challenges and future directions of PCO technology for the elimination of indoor pollutants are compared and summarized.

Keywords: indoor air pollutants; VOC; photocatalysts; environmental conditions; catalyst deactivation



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1. Introduction

Volatile organic compounds (VOCs) are hazardous air pollutants that can be poisonous and mutagenic, and the continued release of VOCs elevates the ozone level of the atmosphere and leads to photochemical haze. VOCs are released by various sources, including electronic devices, construction materials, smoke, consumer goods, occupant-related activities, indoor fuel gas, combustion wastes, and so on [1–3]. Halogenated hydrocarbons, ketones, aldehydes, alcohols, and aromatic compounds are some of the several kinds of VOCs that are used in the industry and normally found in emissions. Consumer goods often result in continuous VOC release and pungent gases like ammonia are released by food wastes, which can markedly lower the well-being of the people in indoor spaces [4,5]. VOCs that are easily diffused and volatile when released into the atmosphere are considered serious contributors to air pollution. These VOCs often generate undesired by-products that can be more hazardous than the parent compound and are associated with serious health risks [6–9].

Adsorption, membrane separation, biological degradation, thermal and non-thermal plasma treatment, and photocatalytic oxidation (PCO) have all been explored so far as means for reducing harmful pollutants in indoor air. PCO has garnered the most interest among all these techniques because of its high success rate in the removal of typical low-concentration indoor pollutants, with maximum efficiency and minimum energy

consumption. Photocatalysis is a promising technology because it can directly convert gaseous atmospheric pollutants (especially VOCs) to less harmful CO_2 and H_2O molecules under optimum conditions. The attractive nature of air cleaning by photocatalysts under UV-visible light has prompted the synthesis of novel nano-catalytic materials for efficient VOC removal [1]. However, photocatalytic oxidation continues to have limitations, such as rapid catalyst deactivation, less efficiency under normal operating parameters, and production of undesirable by-products [3,6].

Conventional semiconductor nanomaterials often have poor pollutant adsorption capabilities at low concentration levels (ppb-ppm) [10]. Numerous studies have shown the potential of TiO_2 as a photocatalyst among various other catalysts (ZrO_2 , SnO_2 , Fe_2O_3 , WO_3 , CeO_2 , ZnS , etc.) owing to its excellent photocatalytic efficiency under UV light irradiation and ideal energy gap between the valence and conduction bands (3.2 eV) [11–14]. TiO_2 catalysts have been synthesized in various morphologies, including nanoparticles, nanotubes, hollow fibers, thin films, and microporous and mesoporous forms. However, TiO_2 normally absorbs wavelengths less than 400 nm, and it is ineffective in enclosed spaces, owing to the lack of visible light absorption capability. Therefore, effective visible light active photocatalysts must be developed for air cleansing applications, especially in the indoor environment [15,16]. Similarly, the deactivation-resistant catalyst also plays an important role in air purification. The synthesis and immobilization of these catalysts on a stable solid support is crucial for superior photo-activity. Reactive intermediates from the breakdown of gaseous reactants may build up on the surfaces of catalysts over time, obstructing the active sites and eventually leading to catalyst deactivation [17,18]. In addition, the photocatalytic effectiveness and by-product generation depends on the operating parameters employed during VOC oxidation. A thorough evaluation of the catalytic activity with a wide range of operating conditions, such as relative humidity (RH), flow rate, light intensity, reactant concentration, and catalyst support, is required to achieve the maximum photocatalytic efficiency for air purification [19–21].

In this review, we focus on two main areas of photocatalytic VOC oxidation: (i) the impact of various operating parameters on catalytic activity; and (ii) photocatalyst deactivation. First, we summarize most of the published articles discussing the effects of various reaction parameters on VOC oxidation. Furthermore, strategies for synthesizing deactivation-resistant photocatalysts, the nature of deactivated photocatalysts, and different techniques for analyzing the extent of photocatalyst deactivation are reviewed and discussed. Finally, the current status and major drawbacks of photocatalytic air purification are discussed, and a few recommendations are suggested for future studies.

2. Air Pollutants and VOCs

Epidemiological studies have shown that exposure to air pollution is the main cause of various unfavorable health effects, including headaches, allergies, and eye irritation. Gaseous particles released into the air by various manmade and natural sources, as well as photochemical transformation processes, make up the complex phenomena known as air pollution [22]. CO_2 , SO_2 , NO_x , particulate matter (1°), NH_3 , CH_4 , volatile organic compounds, and hydrocarbons are classified as primary pollutants, because these compounds have a direct impact on air quality. Examples of secondary pollutants include O_3 , secondary particulate matter, and volatile organic by-products, which are formed by the redox interaction between primary pollutants. Several water contaminants, including heavy metals such as nickel, mercury, and arsenic, can also be present in the air, particularly in industrial areas, where they will lead to fatal illnesses [23].

The most concerning indoor air pollutants (IAPs) are VOCs, which are carbon-containing chemicals that are readily volatile at very low temperatures. VOCs have a vapor pressure higher than 1 mmHg at room temperature, and common examples of VOCs are benzene, toluene, formaldehyde, ethanol, trichloroethylene, etc. These target VOCs in the atmosphere are further categorized into aromatic, aliphatic, chlorinated, and oxygenated hydrocarbons [24,25]. Exposure to VOCs such as benzene and other cyclic aromatic hy-

drocarbons can cause cancer in some individuals; however, a direct link connecting these two has not yet been conclusively proven at typical indoor air concentrations. However, some studies have shown that the risks of cancer are very high under exposure to very low concentrations of these pollutants, with symptoms like headache, drowsiness, weariness, and disorientation [26]. Due to their high bioaccumulation potential and toxic nature, halogenated VOCs are one of the critical classes of indoor air pollutants. Polychloromethanes (PCMs) are the most prevalent and common halogenated VOCs. The remains of water filtration and evaporation systems are the main sources of PCMs, and examples of PCMs include chloroform, dichloromethane, trichloromethane, and carbon tetrachloride. Chlordane ($C_{10}H_6Cl_8$) is another organochlorine VOC that is known to be carcinogenic to humans. It is a white solid, categorized as an organic pollutant and detrimental to human health and environment, just like other chlorinated cyclodiene compounds [27]. Aldehydes make up a sizable portion of all the active VOCs present in the environment, with formaldehyde and acetaldehyde being the important ones [28,29].

Petroleum products, such as gasoline and other fuels made from crude oil, including benzene, toluene, and ethyl benzene, are considered as aromatic VOCs. A considerable quantity of aromatic compounds is released into the environment because of the incomplete combustion of liquid fuels in automobiles. These compounds are also found in a wide range of consumer goods, such as gasoline, paint, drugs, detergents, etc. In addition to being poisonous and cancer-causing, aromatic chemicals can cause serious harm to the ozone layer [30]. Alcohols and ketones constitute another group of VOCs that are frequently found in cosmetics and personal care items, such as hair spray, nail polish remover, cologne, varnishes, paint thinners, and adhesives. Ethyl alcohol, isopropyl alcohol, and benzyl alcohol are examples of common alcohol-based VOCs and ketone-based VOCs include acetone, methacrylate, ethyl acetate, and methyl ethyl ketone [29]. Ethylene is an important organic VOC and when fruits and vegetables are exposed to ethylene during food storage, they undergo physical and chemical transformations, causing food decay. Because of its easy availability and strong solubility, ethylene is widely employed as a solvent in the production of varnishes, resins, adhesives, printing ink, and pharmaceutical products [31]. Table 1 lists the important VOCs and their major indoor sources [32,33].

Table 1. Indoor sources of VOCs.

VOCs	Major Indoor Sources
Toluene	Paints, gasoline, varnishes, solvents, polishes, anti-freezing materials, pesticides
Benzene	Glues, adhesives, detergents, tobacco smoke, gypsum board
Naphthalene	Mothballs, dyes, smoke, insulating materials
Ethylbenzene	Paints, gasoline, inks, glues, candles, insecticides
Chloroform	Solvents, glues, chlorinated water
Ethylene	Food products, gasoline
Formaldehyde	Wood products, wallpaper and paints, flooring items, foam, wallpaper paste, hair conditioners
Tetrachloroethylene	Water repellents, wood cleaners, adhesives, dry-cleaned clothes
Acetaldehyde	Wood products, deodorants, building materials and furnishings, carpets, gypsum
Trichloroethylene	Metal cleaners, adhesives, flooring materials, paint removers
Styrene	Paints, detergents, plasters, adhesives, modelling clay
Acetone	Solvents, sprays, cosmetics, floor coverings, resins, disinfectants, air fresheners

3. Types of Nano Photocatalysts

Semiconducting photocatalysts made of TiO_2 -based nanomaterials continue to form the core foundation of PCO technology, producing a significant number of excited electrons and holes when irradiated with light of suitable wavelengths [34]. Because of the large bandgap (3–3.2 eV), TiO_2 does not work well for all photo-catalytic processes, because it uses only 5% of the total solar energy that impinges on the surface of the earth. Over the past few decades numerous efforts have been made to alter the TiO_2 surface for energy band reduction by doping with elements such as N, C, and S. Researchers have

attempted to develop various hetero-junction catalysts by fusing titanium with metals such as Pt/Pd or with semiconductors like NiO, WO₃, CdS, and quantum dots for improved light utilization [35]. To increase the efficiency of acetone photocatalytic degradation and light absorption, Hu et al. developed a single-atom Au-supported TiO₂ photocatalyst. Similarly, He and colleagues described a method to significantly increase the photocatalytic removal of hydrophilic VOCs (formaldehyde and acetone) from the air by coating hygroscopic periodic acid on WO₃ [36,37]. Sydorenko et al. synthesized transparent TiO₂ thin films and successfully coated them on borosilicate glass by spray pyrolysis. The removal efficiency of the synthesized thin film was tested using acetaldehyde, acetone, heptane, and toluene in 9 ppm VOC mixtures under visible light, and the results showed 100, 100, 78, and 31% conversion, respectively [38].

Materials like SiO₂ have a mesoporous framework (2–50 nm), and these compounds can be used as supports in the synthesis and functionalization of photocatalytic materials. Some advantages of this system are listed below: (1) Pore diameters and structures can be altered at the atomic levels; (2) the pore size makes it easier for reactants to diffuse into the channels and access the active sites; (3) exceptional transparency in the broad UV-visible region provides a photochemically inactive region for the catalyst; (4) with numerous silanol groups in the structure, functionalization with various modifiers is easily achievable [34,39]. Single-site catalysts with tetrahedral geometry are another group of compounds used for photocatalysis. This group includes isolated metal (Ti, V, Cr, and Mo-oxide) moieties with strong solid support, such as mesoporous silica or microporous zeolite. Similarly, replacing Si atoms in the SiO₂ matrix with Ti gives single-site titanium oxide photocatalysts, which can be achieved by several anchoring techniques, including sol–gel method, hydrothermal synthesis, and chemical vapor deposition [39,40].

Another type of metal-free semiconductor used in PCO is graphitic carbon nitride (g-C₃N₄ or CN), which has a bandgap between 2.6 and 2.8 eV. Although carbon nitride is a well-known photocatalyst, its low VB potential is insufficient to produce hydroxyl radicals, resulting in poor activity in terms of VOC degradation. To overcome this, Sun et al. synthesized a g-C₃N₄-based catalyst that was combined with BiVO₄. Under visible light, the toluene conversion rate of BiVO₄/CN was 4.5 times higher than that of the parent carbon nitride [41–43]. Another common carbon-based material used in VOC oxidation is activated carbon fiber (ACF), synthesized from organic precursors through pyrolysis and activation in the presence of carbon dioxide and water vapor. The increased ability of ACFs to absorb VOCs like chloroform and isobutane is attributed to their high specific surface area and superior micro-sized pore volume. Metal-free conducting polymer composites are a cost-effective and environmentally friendly alternative to rGO-based metal oxides/chalcogenides composites for air purification [44–46]. Yan et al. synthesized a novel composite using rGO aerogel and polypyrrole via a hydrothermal process. The result showed that the composite exhibited superior phenol adsorption, owing to the organic nature of the composite material [47].

The formation of electron–hole pairs plays a critical role in semiconductor PCO and requires suitable light energy absorption with the simultaneous promotion of electrons from the valence band (VB) to the conduction band (CB) (as shown in Figure 1). In the following steps, the photogenerated charge carriers combine with oxygen and water molecules to form extremely reactive intermediate species such as hydroxyl radicals. In photocatalytic oxidation reactions, the mass transfer of reactants from the gas phase to the solid phase is crucial. The overall effectiveness and the rate of reaction are significantly impacted for pollutants in the gaseous phase by the net mass transfer from the bulk to the exterior surface of the photocatalyst. Following diffusive mass transfer, the reactive species encounter pollutant molecules at the surface, causing them to break down into compounds with lower molecular weights, which ultimately break down into CO₂ and water [48–51].

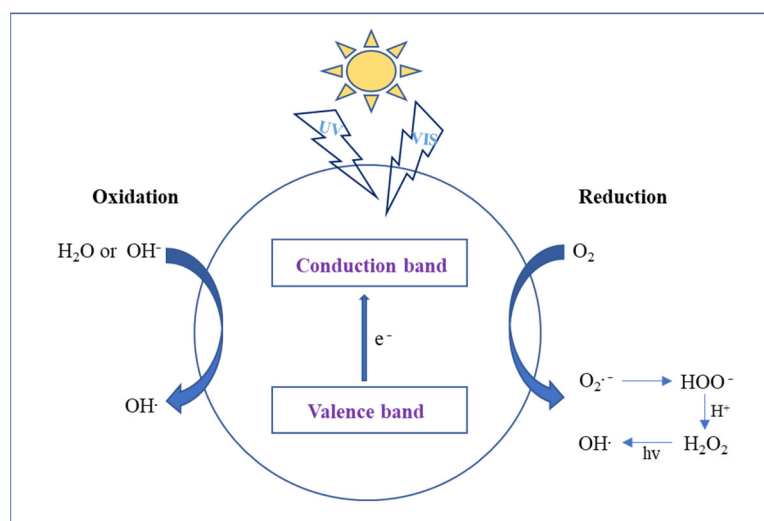


Figure 1. Schematic diagram of electron transfer from CB to VB.

4. Influence of Environmental Conditions

4.1. Effect of Relative Humidity

In recent years, a considerable focus has been given to studying how humidity influences the removal of volatile organic compounds (VOCs) with different photocatalysts. The surface-bound water molecules and OH groups produced by the dissociative chemisorption of moisture on the catalyst surface can be quite important in the photo-oxidation of VOCs. In the total absence of water vapor, the complete mineralization to CO_2 does not occur and the photocatalytic breakdown of organic compounds like toluene or formaldehyde is significantly slowed down. However, as water molecules start occupying more and more active sites, the reaction rate decreases, because of the considerable build-up of water vapor on the catalyst surface. Therefore, finding an optimal level of humidity is a crucial step in photocatalytic reactions [52].

The photo-oxidation in a dry atmosphere as well as under higher humidity conditions was usually less effective. Quici et al. found that the ideal humidity levels for the breakdown of toluene both with and without a photocatalyst are around 10% RH. Thevenet et al. observed a continual decline in the reaction rate with a rise in humidity for the photocatalytic oxidation of a relatively high concentration of acetylene (1000 ppm) [38]. This trend, however, cannot be generalized for all reactants or with different experimental setups. For example, Durme et al. showed a higher conversion rate for toluene (500 ppb) at 26% RH by non-thermal plasma treatment, which is a complementary method for gas-phase PCO [53,54]. Korologos et al. investigated the effects of water vapor concentrations on the photo oxidation of benzene, toluene, ethylbenzene, and *m*-xylene (BTEX). The effect of humidity on the PCO showed strong dependence on the type of the BTEX and the water vapor content. The increase in residence time resulted in a significant increase in the conversion for every compound [55].

Humidity has both beneficial and detrimental effects on the ability of TiO_2 photocatalysts to catalyze reactions. For example, the total oxidation of toluene to CO_2 is increased at higher humidity levels because of the production of hydroxyl radicals, after which the catalytic activity becomes stable over time. However, then the VOCs would face competition from the high water content in the atmosphere, which can decrease the selective adsorption, and thereby reduce the rate of reaction [56]. Like toluene, the amount of moisture had a similar impact on the rate at which formaldehyde is oxidized. The oxidation rate increased to a maximum when the humidity level was gradually raised, and then the rate was decreased with a further rise in the water vapor concentration [57]. Assadi et al. performed VOC oxidation of trimethylamine and isovaleraldehyde and observed the impact of humidity on the degradation rate. Water vapor can enhance the degradation through the

formation of OH^\bullet radicals when the humidity level is less. But as the water vapor content increases, competition between water vapor and VOCs for the active sites at the surface increases, and as a result, the rate of degradation slows down. From the experiments, the ideal RH levels for isovaleraldehyde and trimethylamine were found to be 40 and 25%, respectively [58]. Vildoza et al. performed photo-oxidation of 2-propanol-toluene mixtures at indoor air concentrations at two different relative humidity values (0 and 60%) at 25 °C using a TiO_2 catalyst. The study showed that (1) the competition of 2-propanol-toluene binary mixture with water vapor for active sites is insignificant under dry conditions, (2) the lesser the solubility of the organic pollutant, the more the inverse impact of humidity on the adsorption of the pollutant on the TiO_2 surface, and (3) the degradation of VOC increases with a decrease in water vapor content, with the maximum conversion achieved at 0% RH [59].

Along with the impact on degradation efficiency, RH can also play a major role in the selectivity of products and the types of by-products formed during PCO. According to Vincent et al., a high relative humidity (30%) has a favorable impact on the conversion of 1-propanol while also stifling the production of unwanted by-products (such as propionaldehyde) owing to the higher OH radical concentration at higher humidity levels [60]. Different results were obtained when Debono et al. studied the degradation of decane and observed that water vapor slows down the removal of unwanted impurities and drastically increases their quantity around the catalyst surface [61]. The above findings were further supported by the oxidation of binary mixtures of 2-propanol and toluene. Higher humidity levels led to significant loss of overall conversion (40 to 70%), with a varying initial concentration ratio of 2-propanol to toluene [59]. Kibanova et al. showed that the photo-oxidation of formaldehyde was affected by the competition between water vapor and reactants for active sites. They compared the performance of clay- TiO_2 nanocomposites to the reference catalyst P25 under controlled conditions of RH [62] and the results are shown in Figure 2.

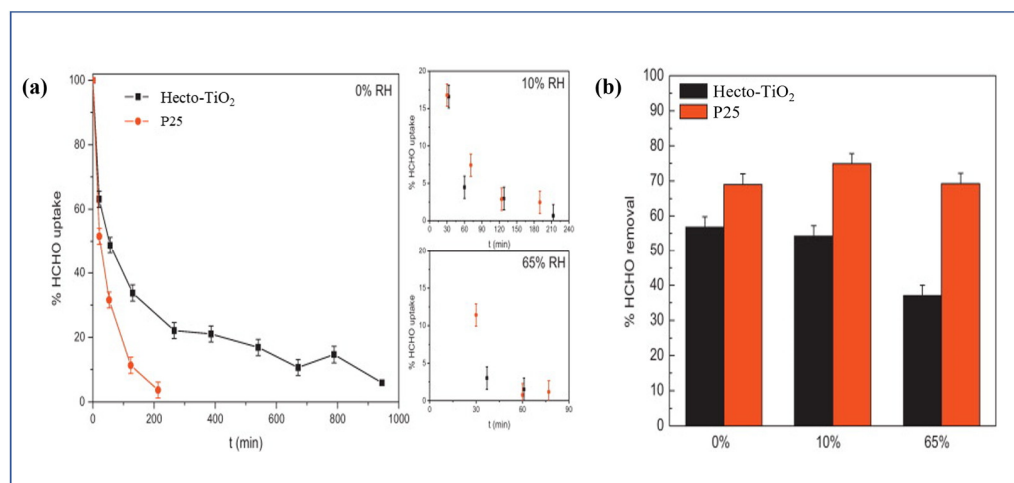


Figure 2. (a) Formaldehyde uptake under 0, 10, and 65% RH. (b) Percentage of formaldehyde removal with RH. Reproduced with permission from [62]. Copyright 2012 Elsevier Ltd.

The nature of water to compete with reactants can considerably diminish the ability of catalysts to adsorb VOCs. However, selective sorption of VOCs to water vapor can be accomplished by hydrophobically altering the catalyst surfaces. According to Yu et al., increasing the RH (30–70%) enhances the catalytic oxidation of toluene more than that of formaldehyde, presumably because toluene is more hydrophilic than formaldehyde [62,63]. Figure 3a shows the impact of relative humidity on toluene degradation efficiency. Even though the photocatalyst and pollutant remain the same, no specific pattern was observed in these experiments. Instead, the conversion rate was found to mostly depend on the operating parameters employed in each study [51].

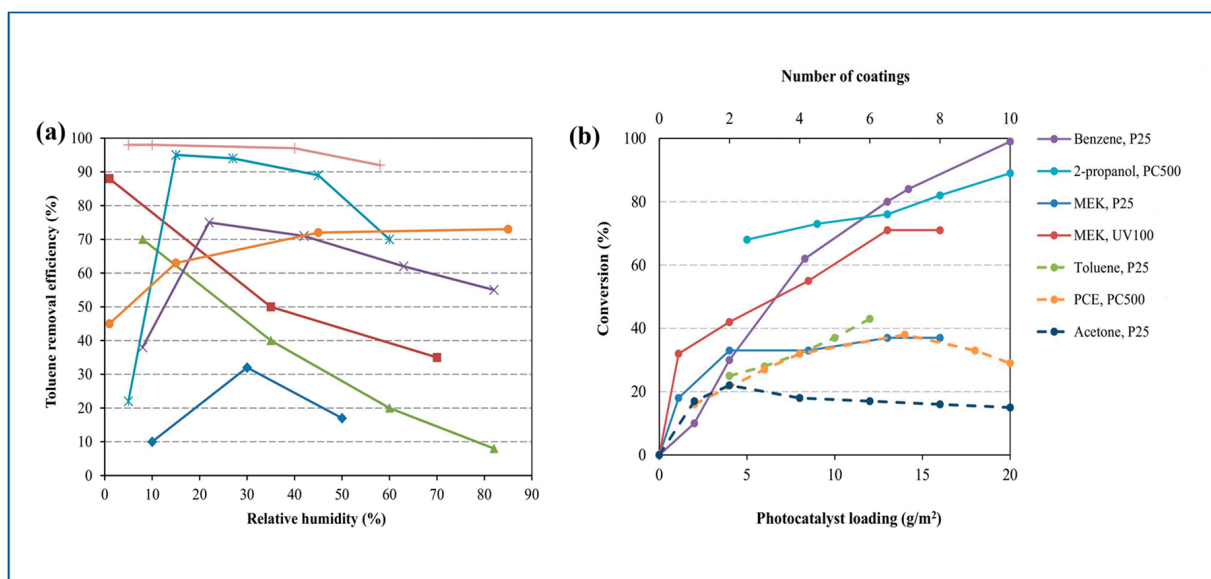


Figure 3. (a) Effect of RH on the toluene removal rate using the P25 catalyst. (b) Impact of catalyst loading on VOC conversion rate. Reproduced with permission from [51]. Copyright 2017 Elsevier Ltd.

4.2. Effect of VOC Type and Concentration

The type of reactants (VOCs) used and their inlet concentration considerably affect the PCO of air pollutants. There is a widespread acceptance that increasing VOC concentrations would lead to lower removal efficiency for different classes of VOCs [51]. Mamaghani et al. performed VOC oxidation using commercial TiO_2 catalysts to study the impact of various operational parameters. It was found that the target pollutant's removal rate is always greater at lower concentrations (100 ppb) than at higher concentrations (1 ppm). This is because, at higher VOC concentrations, the ratio of reactive species to VOC molecules decreases, because of which a large portion of VOCs remains unreacted. They compared the removal efficiency of toluene and methyl ethyl ketone (MEK) and observed that on almost all titania catalysts, the MEK removal rate was lower than that of toluene. One possible reason given for the high reaction rate of toluene is the better interaction of toluene with the intermediate OH radicals, which leads to a higher removal efficiency [19]. The same group of researchers studied the effect of MEK inlet concentration over various titanium catalysts, and like previous results, the VOC removal rate was decreased with an increase in the inlet concentration (Figure 4a). This was expected, given that, when the inlet concentration increases, the proportion of active sites to the incoming MEK molecules drops. Thus, MEK molecules are prevented from participating in the degradation mechanism. Figure 4b illustrates the concentration of by-products produced during the VOC oxidation with various MEK inlet concentrations. A potential reaction route is shown in Figure 4c, based on the products/by-products formed in the PCO of MEK [64].

Jafarikoju et al. performed PCO of toluene and the data showed that the conversion fell from 37 to 27% when the initial concentration of toluene increased from 20 to 100 ppm. Similarly, Mo et al. found that raising the inlet concentration of toluene from 1 to 4 ppm caused a 30% reduction in the breakdown efficiency of toluene [51]. According to Yu et al., rate constants of toluene, *p*-xylene, and *m*-xylene are linearly related to their hydroxyl radical reaction rate constants. In a different work, Vildoza et al. demonstrated that the mineralization rate of 2-propanol was reduced from around 90 to 63% by raising the initial concentration of 2-propanol from 100 to 700 ppb [65]. Through their study, Boulamanti and Philippopoulos established the following order for the VOC oxidation rate of alkanes: *n*-pentane < *i*-pentane < *n*-hexane < *i*-hexane < *n*-heptane. Based on this progression, they hypothesized that branched alkanes had a higher reaction rate because they possess a tertiary carbon atom [66,67].

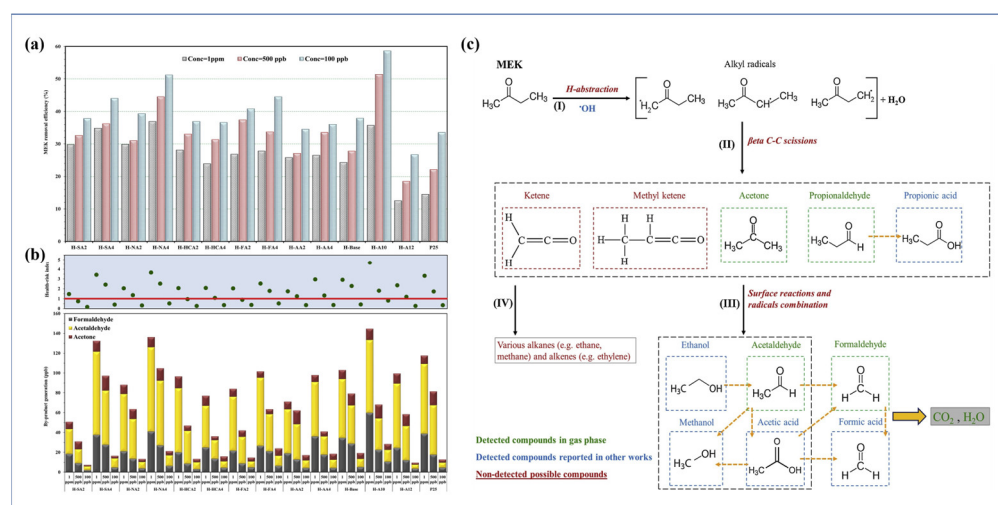


Figure 4. (a) Influence of inlet concentration on MEK oxidation. (b) By-products formation over various MEK inlet concentrations. (c) Predicted reaction route for the PCO of MEK. Reproduced with permission from [64]. Copyright 2019 Elsevier Ltd.

For aromatic compounds, the removal efficiency increases in the following order: benzene < toluene < *o*-xylene < ethylbenzene over bare P25, and benzene < *o*-xylene < ethylbenzene < toluene over the P25/AC catalyst. This result suggests that the presence of activated carbon on TiO₂ affects the conversion of toluene more than that of any other aromatic hydrocarbons [68]. According to Li et al., the catalyst activity dropped from 93 to 24% when the initial toluene concentration increased from 200 to 1000 ppb. Similarly, the adsorption amount of toluene on the g-C₃N₄/TiO₂/ACF catalyst decreased with an increase in the initial concentration of toluene. Thus, the reaction rate is maximum when the number of reactant molecules is less than or equal to the number of active sites on the catalyst. After the photocatalyst reaches its maximum capacity, the initial concentration does not affect the rate of reaction anymore [2,69]. So far, researchers have found that a higher initial VOC concentration can increase the number of adsorbed pollutants on the catalyst surface. However, once the initial concentration reaches a saturation point where there are not enough oxidation radicals and active sites on the catalyst to carry out further oxidation, more and more reactants will depart the reactor without engaging in the photo-oxidation reaction [2,70].

4.3. Effect of Catalyst Loading and Support

In PCO reactions, a support material is often employed to increase the adsorption capacity and decrease the aggregation of nanoparticles on the photocatalyst surface. PCO efficiency is considerably influenced by the catalyst loading amount and the kind of support material used [2]. Increasing the amount of catalyst loading can improve the reaction rate by reducing the adsorption competition, increasing the surface area, and increasing the availability of the active sites of the catalysts. However, studies have indicated that when catalyst loading exceeds a particular threshold, the degradation rate decreases. This is attributed to the reduced light exposure and agglomeration of particles produced by the large amount of catalyst loading [71].

It is desirable to increase quantum efficiency by immobilizing the catalyst on a support material with suitable properties, like high surface area, porous structure, strong transparency, and stability under UV irradiation. One common support used in many projects is activated carbon (AC), which improves the retention of VOCs on catalytic beds by lowering the competition of water vapor to reactants [51]. Using AC with P25 might nullify the effects of A short residence time and excess humidity on the degradation of pollutants in the oxidation of aromatic VOCs and formaldehyde [68,72]. Li et al. synthesized a novel composite by combining a charcoal skeleton and “chrysanthemum” g-C₃N₄ (C/CN-x). The

catalyst was used for the visible-light-induced breakdown of formaldehyde and the most effective photocatalytic material was found to be C/CN-8, with a removal rate of 84.63%, which was 130% more effective than the conventionally used g-C₃N₄. The favorable result is mainly due to the high surface area provided by the catalyst support material [73]. Liu et al. performed PCO of benzene with Ti³⁺ self-doped TiO₂ and found that the photocatalytic activity of benzene was largely improved with doping. The insertion of Ti³⁺ into TiO₂ microspheres decreased the electron–hole recombination and enhanced the light absorption ability, thereby increasing the photocatalytic efficiency of the catalyst. Figure 5a shows the rate of benzene oxidation with Ti-doped TiO₂ catalyst at various calcination temperatures. The possible mechanism of the degradation reaction is given in Figure 5b. CO₂ and CO are the major products formed during the reaction (Figure 5c,d) [74].

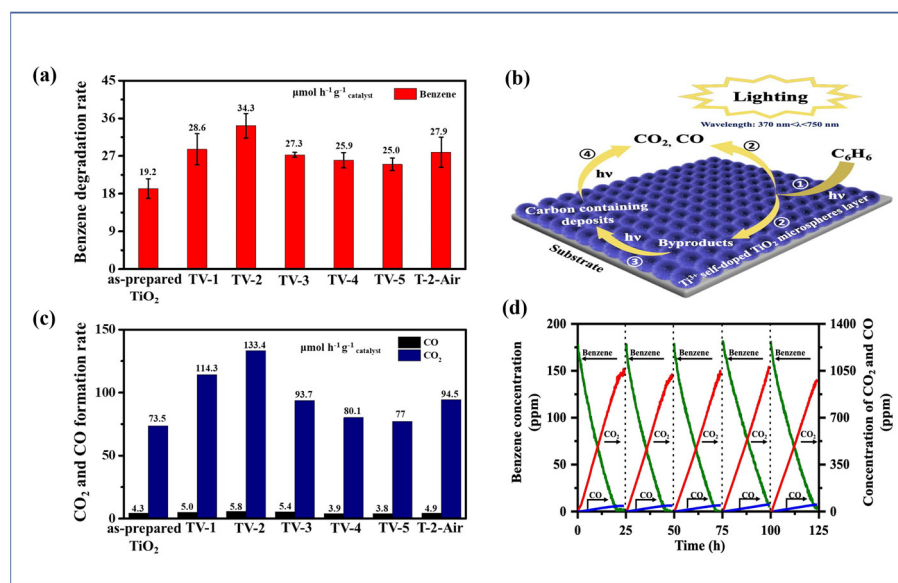


Figure 5. (a) Benzene oxidation rate at various calcination temperatures. (b) Probable mechanism of benzene oxidation. (c) Product formation rate at different calcination temperatures. (d) Repeated cycles of PCO of benzene on TV-2 catalyst. Reproduced with permission from [74]. Copyright 2020 Elsevier Ltd.

Using pure aerolyst 7710 pellets coated on TiO₂ glass beads as photocatalysts, Verbruggen et al. examined the oxidation reaction of ethylene. A significant increase in ethylene removal efficiency (up to 70%) was observed for TiO₂-coated glass beads when compared with the parent catalyst. The support provided enhanced light scattering and increased the interaction time between the reactants and photons, thereby increasing the reaction rate [75]. To increase the stability and efficiency of the photocatalyst, a binder is often used while depositing the photocatalyst on the support material. Thevenet et al. used a silica binder to attach P25 on organic fibers and demonstrated that the conversion rate was substantially lower with the binder present, and vice versa [76]. Mo et al. synthesized TiO₂ with silica and mordenite as the support and observed a higher adsorption constant for P25/silica composite because of the strong adsorption capability of silica. The enhanced surface area improves mass transfer; therefore, the activity of the catalyst can be improved by adding a suitable support material [77].

4.4. Effect of Light Intensity

The energy needed to initiate the PCO reaction is provided by UV-visible light, and it is the first step in the activation of the photocatalyst. Theoretically, wavelengths less than 380 nm can activate the TiO₂ photocatalyst, which is equivalent to the bandwidth of TiO₂ (3.2 eV) [71]. Electrons in the valence band of TiO₂ are excited by a UV source,

and the frequently used light sources in PCO reactions are fluorescent black-light lamps (300–400 nm) and germicidal lamps (UVC, 254 nm). Another common light source used is UV light-emitting diodes (365 nm) due to their long lifespan and excellent performance. Also, a comparison study of photo oxidation of several VOCs revealed that the two light sources, black light and germicidal lamp, with the same power showed no significant performance difference between them [4,51]. When the light intensity is increased, more photons will be formed and, as a result, more e^-h^+ pairs will be generated, which will increase the oxidation rate. For example, the PCO of TCE and 1-propanol both moved from the first-order to half-order rate when the light intensity is increased from 1.5 to 4 W/m². Although increasing the light intensity can enhance the pollutant removal rate, excessive light reduces the quantum efficiency and creates unwanted energy loss [51,60,78].

According to Kibanova et al., toluene oxidation over a P25 catalyst was finished nearly twice as quickly by utilizing an ozone-producing lamp as opposed to a UVA-generating lamp [79]. Studies on the photo-oxidation of formaldehyde, toluene, and benzene over P25 showed that the degradation rate follows the order of UVC/O₃ > UVC > UVA. That is, the low-energy photons and ozone of UVA play a positive role in PCO reactions of VOCs [53,62,80]. The same has been confirmed by Krichevskaya et al. by the PCO of a mixture of VOCs. Thus, the amount of CO₂ produced during the reaction increased from 7 to 20 ppm when the O₃ concentration in the chamber was increased from 40 to 80 µg L⁻¹ [81]. Increasing the light intensity at the catalyst surface or utilizing a shorter wavelength light source generally improves the removal efficiency of VOCs. The generation of intermediates or by-products, as well as catalyst deactivation, can also be controlled using the appropriate light sources with optimal intensity [51].

Table 2 highlights how various reaction conditions affect the removal efficiency of photocatalysts in VOC oxidation reactions.

Table 2. Effect of operating parameters on VOC oxidation.

Catalyst	VOC Type	Concentration	RH (%)	Light Source	Removal Efficiency (%)	Ref.
TiO ₂ /diatomite composite	Acetone, MEK	10 ppm	15	UVA lamp	~42–61	[82]
TiO ₂ thin film	Acetone, toluene, <i>p</i> -xylene	0.1–0.3 mol/m ³	35	UV lamp	~55–77	[83]
C-doped TiO ₂	Toluene	150 mg/m ³	60	Visible light	~60	[84]
TiO ₂ /Mg-Al LDH	Toluene	100 ppm	50	UV lamp	~74	[85]
Pt-TiO ₂	MEK	1 ppm	100	UV lamp	~73	[86]
CNT-TiO ₂	Gaseous styrene	25 ppm	0	UV-LED light	~50	[87]
Pt-TiO ₂ -R	<i>m</i> -xylene	1 ppm	50	UV lamp	~73	[88]
Ce-TiO ₂	Toluene	150–600 ppb	<3	Visible light	~22	[89]
Pd/WO ₃	Acetaldehyde	5 ppm	50	Fluorescent-visible light	~99	[90]
Pt-TiO ₂	BuAc	1 ppm	100	UV lamp	~98	[86]
TiO ₂ /diatomite composite	2-Heptanone	10 ppm	15	UVA lamp	~38	[82]
MOF(Ti)	Acetaldehyde	200 ppm	80	Visible light	~98	[91]
TiO ₂	Ethanol	200–2000 ppb	9–60	UVC lamp	~4–44	[92]
SiO ₂ coated TiO ₂	Isoflurane	500 ppb	50	UVC fluorescent lamp	~100	[93]
N-doped TiO ₂	Ethyl benzene	20–140 ppm	50	TUV lamp	~25–100	[94]
F-TiO ₂	Toluene	30 ppm	50	VUV lamp	~80	[95]
Zn-Ti-LDH	Toluene	500 ppm	50	UV lamp	~75	[96]
MOF(Fe)/Fe ₂ O ₃	<i>o</i> -xylene	25 ppm	50	Xenon lamp	~100	[97]
GO/ZnO	Benzene	100 mg/L	35–45	UV lamp	~87	[98]
Zn ₂ SO ₄ /LDH	Toluene	500 ppm	60	UV lamp	~90	[99]

5. Catalyst Deactivation and Possible Solutions

5.1. Main Reasons for Catalyst Deactivation

Prolonged irradiation and periodic uses cause the rapid loss of activity of the photocatalytic materials used for VOC destruction. In contrast to the liquid–solid interface catalytic reactions, photocatalytic processes occurring at the gas–solid interface normally show a steady decline in the activity over time. The wetting ability of liquid can keep the catalyst surfaces fresh, whereas the air medium is unable to offer the same cleaning property. Hence, photocatalysts operating in the air are more vulnerable to deactivation [100]. Intermediates are formed on the surface of the catalysts during VOC oxidation, and many of them interact more strongly with the catalyst than the initial reactant molecules. The deposition of these intermediates on the catalyst surface blocks the photons and prevents the active transfer of O_2 and other reactive species onto the surface of the catalyst. Einaga et al. showed that the effectiveness of VOC removal is drastically decreased after 2 h of photoirradiation of organic compounds like toluene, benzene, cyclohexene, and cyclohexane [101]. According to Taranto et al., the methanol degradation rate was largely reduced over the P25 catalyst immobilized on cellulose fibers at high irradiance (108 W/m^2). They proposed that since cellulose is susceptible to UV radiation, it is likely that the by-products of the reaction will compete with the reactant for the active sites and eventually slow down the reaction rate [102].

One of the most common reasons for the photocatalyst deactivation is the adsorption of chemical intermediates on the catalyst surface. Thevenet et al. used a liquid-phase acidic extraction technique and identified that formic acid, oxalic acid, and acetic acid were adsorbed on the TiO_2 surface during the photo-oxidation of acetylene. They concluded that the accumulation of these carboxylic acids was the primary cause of catalyst deactivation [103]. In a similar work, Einaga et al. observed the evolution of CO_x from the P25 catalyst regeneration process during the oxidation of cyclohexane, cyclohexene benzene, and toluene. They summarized that carbon residues formed from the aromatic compounds were more resistant to oxidation than those from the non-aromatic compounds [101]. Another important finding in VOC oxidation is that the degradation of hydrophobic molecules can be severely hampered by the binding of interfering molecules with hydrophilic properties (such as acetone or benzaldehyde) on the TiO_2 surface [36]. Hay et al. showed that the deactivation of the photocatalyst was caused by the production of a silica layer from photo-oxidation of siloxanes, which clog the pores of P25 in ambient air at low concentrations [104].

Cha et al. showed that half-oxidized organic compounds with low volatility bind to the TiO_2 catalyst surface, hindering the efficiency of air purification in the PCO of toluene [105]. Benzyl radicals are produced during toluene degradation and are further oxidized to produce benzyl alcohol or benzaldehyde. In the presence of superoxide radicals, benzoic acid can be produced selectively, which can then dimerize into benzyl benzoate. High molecular weight polymeric compounds could be produced during this process, which could effectively close the active center of the catalyst, thereby impeding photocatalytic reactions [106]. Relative humidity also plays a significant role in photocatalytic deactivation, and it can affect the extent of deactivation by (1) replacement of hydroxyl groups on the photocatalyst surface by water molecules and (2) absorption of water molecules on the photocatalyst surface, preventing VOC molecules from accessing the active sites [107].

5.2. Properties of Deactivated Photocatalysts

The nature and characteristics of a deactivated photocatalyst often differ from those of a fresh catalyst. For example, when a TiO_2 catalyst undergoes fouling during VOC oxidation, the primary change is that the color of the catalyst turns from white to pale brown. Hay et al. confirmed the formation of silica on the catalyst surface with TEM and electron microprobe techniques for VOC oxidation reactions [18,104]. Analysis using electron microscopy can validate the extent of photocatalyst deactivation. Elemental mapping using TEM electron energy loss spectroscopy (EELS) can be used for the detection

of carbon remaining on deactivated TiO_2 after various cycles of VOC oxidation. Carbon deposits on the photocatalyst surface can be calculated by measuring the concentration of CO_2 formed during the photodegradation reaction in clean airflow. Einaga et al. performed photoreaction of several VOCs with constant UV irradiation for 2 h in a continuous flow reactor. The amount of CO_2 produced from the oxidation of cyclohexane and cyclohexene was much less when compared to the CO_2 formed from the oxidation of benzene and toluene. That is, the photodegradation of benzene and toluene deposits more carbon on the TiO_2 surface, thereby resulting in the faster deactivation of the catalyst [101]. In a similar study, the amount of CO_2 that evolved from the F- TiO_2 /Pt catalyst was significantly lower than that of pure TiO_2 , indicating that the former was more deactivation resistant during the breakdown of toluene. The amount of CO_2 formed from the used photocatalyst surface can be considered as an indicator of the extent of photocatalyst deactivation [107].

In a different work, Chen et al. investigated the intrinsic causes of VOC-mediated intermediates deposition on TiO_2 (P25), in combination with the findings of experiments and DFT calculations. They used $\beta\text{-Ga}_2\text{O}_3$ as a model catalyst with enhanced reactant adsorption to prevent the deactivation of the catalyst during VOC oxidation reactions. The efficient ring-opening abilities of the intermediates on the surface of the $\beta\text{-Ga}_2\text{O}_3$ catalyst increased the durability and achieved excellent resistance to deactivation during the prolonged VOC oxidation process (Figure 6) [108]. In contrast to these findings, several studies have asserted that there has not been any significant photocatalyst deactivation after various VOC oxidation cycles. For example, Verbruggen et al. reported that throughout the 30 h of oxidation, there was no real reduction in the conversion rate of acetylene over P25 and PC500 catalysts. Similarly, Taranto et al. proved that the degradation efficiency of methanol and *n*-octane over titanium catalysts remained the same for an entire day's operation [109,110].

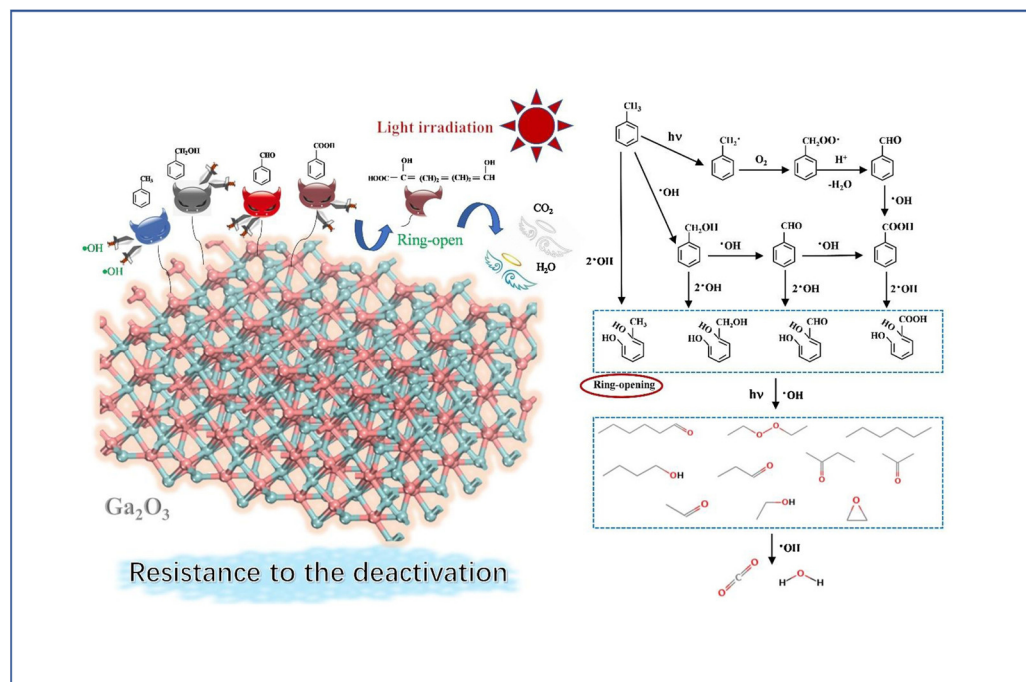


Figure 6. Schematic representation of intermediate formation and reaction mechanism of PCO of toluene on $\beta\text{-Ga}_2\text{O}_3$ catalyst. Reproduced with permission from [108]. Copyright 2020 Elsevier Ltd.

5.3. Solutions for Reducing the Catalyst Deactivation

There are two possibilities once a photocatalyst reaches its limiting point: replacement and regeneration. Since catalyst replacement is not an economically viable option, regeneration techniques have been studied most often. Long-term exposure to air, use of UV

radiation, treatment with vaporized H_2O_2 solution, plasma treatment, and ozone purging in the presence of moisture are some of the methods used for catalyst regeneration [51].

UV cleaning has been employed as a post-treatment method in some studies to overcome catalyst deactivation caused by heteroatoms containing VOCs. However, after UV cleaning, the photocatalytic activity was not entirely restored, and the regeneration of the catalyst was influenced by light intensity and illumination duration. For example, a UV cleaning process involving a low-power (8 W) UV lamp was unable to completely restore the activity of the catalyst used to degrade benzene, whereas a UV cleaning experiment using a 16 W light was successful in doing so (Figure 7) [111]. Numerous studies have used heat treatment as a post-treatment method to entirely convert carbonaceous deposits on the catalyst surface into CO_2 . Here, the catalyst surface must be heated above the typical vaporization temperature of VOC molecules to break the strong bonds between the catalyst and the organic deposits. However, severe heat treatment can cause the phase transition from anatase to rutile phase in the TiO_2 catalyst and reduce the surface hydroxyl groups, which in turn will cause a decrease in the photocatalytic activity [101].

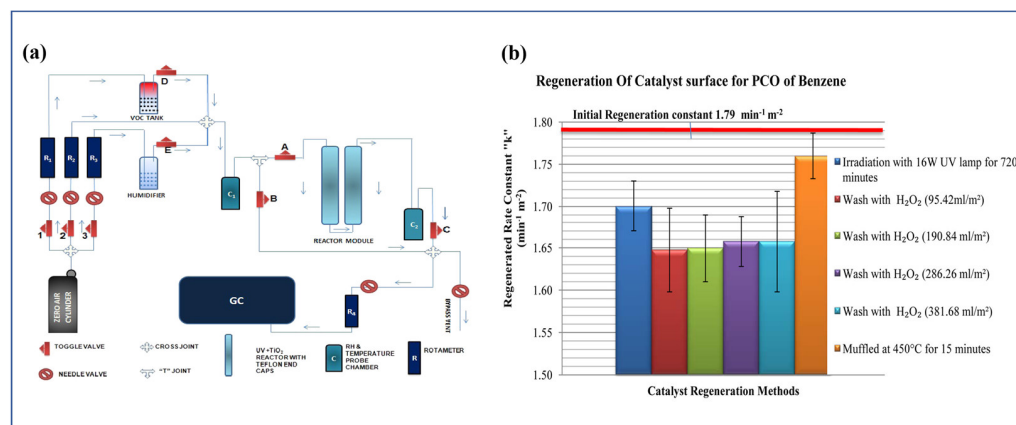


Figure 7. (a) Schematic diagram of a photocatalytic reactor used for VOC oxidation. (b) Catalyst regeneration rate with different post-catalytic treatments. Reproduced with permission from [111]. Copyright 2015 American Chemical Society.

Another common solution for reducing photocatalyst deactivation involves cleaning the surface of the used photocatalyst with an aqueous solution, and the effectiveness of the regeneration depends on the washing conditions. For example, washing the catalyst with NaOH is a useful technique to get rid of the surface SiO_x residues created during the oxidation of siloxane [112,113]. One potential technique for the prevention of catalyst deactivation is the combined use of adsorbents with photocatalysts. In this way, pollutants are first absorbed by the adsorbent molecules and, additionally, the adsorbent may hold onto the intermediate species generated during the photocatalytic oxidation so that they can be further oxidized without affecting the active sites of the catalyst [114,115]. Arana et al. evaluated the oxidation of gaseous alcohols on TiO_2 and AC- TiO_2 composites. While AC- TiO_2 showed no signs of deactivation, pure TiO_2 lost its activity during mineralization of methanol and ethanol. But the opacity of activated carbon restricts its applications [116]. By the direct incorporation of TiO_2 in $\text{NH}_2\text{-UiO-66}$, Yao et al. created a TiO_2/MOF nanocomposite with enhanced degradability and durability. The catalyst was used in the degradation of styrene and the residence time of the reactant was extended by the highly porous MOF, which reduced the deactivation of the catalyst. In a similar work, Suárez et al. used sepiolite, a common clay mineral to combine with TiO_2 to create a hybrid composite material. The composite exhibited excellent mineralization efficiency by absorbing the undesirable TCE degradation intermediates such as dichloroacetyl chloride and phosgene during the PCO reaction [117,118].

In another work, Krichevskaya et al. considerably reduced the time needed to restore P25 activity from hours of post-treatment (15 h) to a relatively shorter time (20 min) with the utilization of UVA + O₃ treatment at high temperature (180 °C) [66]. Additionally, TiO₂ in the form of dispersed powder and thin films showed enhanced VOC degrading activity compared to pellets and honeycomb structures. Thus, a high TiO₂ surface area and enhanced light absorption were achieved with powdered and film forms of TiO₂ [119,120]. Due to its distinctive ordered open-channel structure, TiO₂ nanotubes (TNTs) have shown a great deal of promise in the making of the deactivation-resistant photocatalyst. TNT surfaces are largely exposed to reactants compared with other forms of TiO₂ catalysts which make it easier for the gas molecules to diffuse through the surface. Because the intermediates are immediately destroyed in the presence of oxygen, the development of carbonaceous intermediates on the surface of TNTs can be prevented during the oxidation of VOCs [18,107]. Weon et al. studied the catalytic efficiency of TNT and TiO₂ nanoparticles (TNP) during the PCO of toluene and acetaldehyde. The color change of fresh and used catalyst was visible (Figure 8a) and during post-catalytic treatment, CO₂ was released from the catalyst surface (Figure 8b). The durability of TNT was excellent even after five repeated cycles of toluene oxidation compared to TNP, and the results are shown in Figure 8c,d [18].

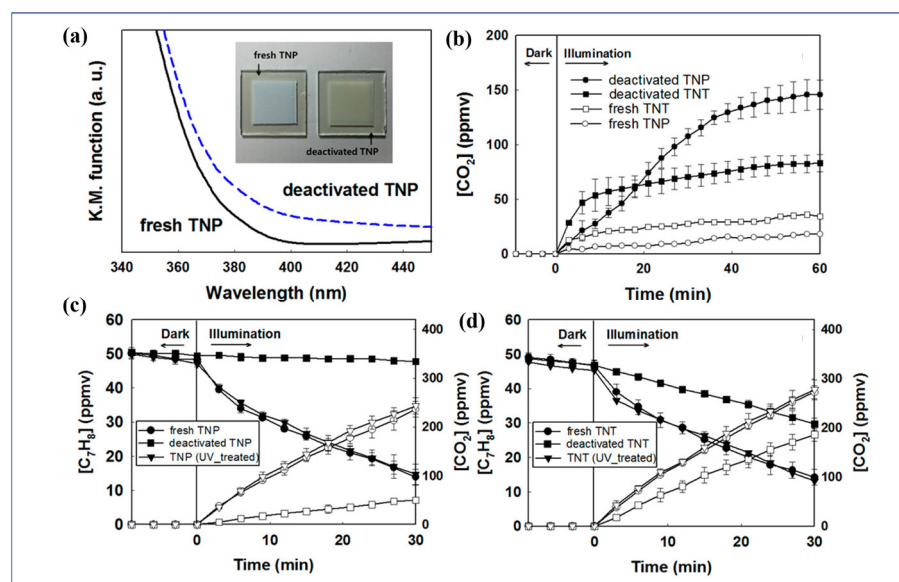


Figure 8. (a) Diffuse reflectance UV-visible spectra of fresh and deactivated TNP catalyst. (b) CO₂ formation rate from fresh and deactivated TNP and TNT catalysts. (c) Profile of PCO of toluene with TNP catalyst. (d) Photocatalytic oxidation rate of toluene using TNT catalyst. Reproduced with permission from [18]. Copyright 2016 American Chemical Society.

6. Conclusions and Outlook

The recent developments in the PCO technology for the removal of atmospheric pollutants are assessed in detail in this review. Compared with various other kinds of pollution, air pollution has more sources, and it spreads very quickly, making it difficult to control. Thus, in a polluted atmosphere, especially in indoor environments, air pollution control and prevention present numerous problems. Photocatalysis is actively being researched as a potential air cleansing method. It has been particularly well suited for indoor air purification since it breaks and converts harmful pollutants into CO₂ and H₂O under ambient operating parameters. TiO₂, the most investigated photocatalyst for air purification, does not absorb visible light, and the efficiency of the photocatalyst depends on various external operating parameters. In addition, leaching and deactivation of the photocatalyst are major issues faced during the practical application of PCO but have not received much research interest. Although considerable progress has been made in the

use of nano-catalysts for the photocatalytic degradation of VOCs, several issues must be resolved before this technology can be put into practice in various fields. Novel catalytic materials have found applications in photocatalytic reactions, but to replace TiO₂ based catalysts with novel materials in practical applications still has a long way to go.

Based on the recent developments in PCO technology, the following conclusions were drawn and several directions for future development are provided. Some of the important challenges and areas of improvement are as follows:

- (1) The photocatalytic efficiency of VOC oxidation depends on various operational parameters (airflow, reactor type, residence time, wavelength and intensity of light, humidity, temperature, etc.). To understand how the degradation efficiency depends on various external factors and to achieve the maximum conversion rate, it is always recommended to perform the PCO reaction in a standard reactor system with different operational parameters.
- (2) The stability of the investigated photocatalyst is demonstrated by how long it lasts until the activity starts reducing during continuous operation. The important questions are why the deactivation occurs and how we can reduce the deactivation.

In brief, optimizing reaction conditions and preventing catalyst deactivation could maximize the efficiency of the photocatalyst used for air purification. Photocatalytic oxidation techniques can be a potential solution for effectively eliminating indoor air pollutants. However, with the current progress in VOC oxidation, the commercialization of this technology would be difficult. Considering this, photocatalysis should be an upgraded technique and the catalytic nanomaterials synthesized for the removal of atmospheric VOCs under realistic conditions should be the focus of substantial scientific research in the near future.

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