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A “deactivation” kinetic model for predicting the performance of photocatalytic degradation of indoor toluene, o-xylene, and benzene

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ABSTRACT

A glass-plate reactor coated with a commercial titanium dioxide was used to investigate the performance of ultraviolet photocatalytic oxidation (UV-PCO) of toluene, o-xylene and benzene contained in air. The concentration of each compound at reactor inlet ranged from 0 to 3.5 ppm. Under indoor air conditions, the degradation rate of toluene and o-xylene rose to a maximum value with the concentration increase, and then began to decrease. This could not be interpreted by the classic L–H model. Considering the possibility of the photoactivity decay, a “deactivation model” fitted for the concentration levels tested. Studies found that the degradation performance of benzene also worked well with this model. Besides, the concepts of active region, deactivation region, inhibiting concentration, maximum reaction rate, and maximum required light intensity were applied to explain the phenomena. The results would be useful for better understanding the reaction kinetics of PCO in deactivating common indoor air contaminants.

1. Introduction

Previous surveys show that people spend about 87% of their life time indoors [1]. Poor indoor air quality (IAQ) can significantly affect people’s health, comfort, satisfaction, and productivity. Volatile organic compounds (VOCs) are an important class of pollutants in indoor air. A long-term exposure to VOCs can be detrimental to human health causing sick building syndrome [2,3]. VOC may cause offensive odors, skin and membrane irritations, allergic reactions, and chronic effects including cancer [4,5]. Applying ultraviolet photocatalytic oxidation (UV-PCO) to reduce indoor VOC contaminants and improve IAQ has received increased attention in recent years [6–8].

The Langmuir–Hinshelwood (L–H) rate models (unimolecular or bimolecular) are often used to describe PCO kinetics [7–10]. Ignoring the effect of competitive adsorption of water molecules, photocatalytic degradation reaction of VOC can be described by a unimolecular L–H model at low concentrations [5,7,8]. For indoor applications, it is generally assumed that the contaminants are at sufficiently low concentrations ($<$1 ppm) to be in the linear range of the L–H curve for surface coverage and thus the reaction is pseudo first-order [9,10]. However, it may be possible that a PCO reactor has to work with an indoor concentration level at several ppm, such as immediately after painting a building. If the L–H model is applied through, with increasing initial VOC concentration, reaction rate will rise, and ultimately is close to the value of reaction rate constant [11,12]. However, experimental results have indicated that this is not true, especially at relatively high concentration levels. As the reaction speeds, the amount of intermediate products also increases in the photocatalytic degradation process. It is inevitable that catalyst deactivation will occur when a lot of intermediate products have been adsorbed on the catalyst surface [13,14]. Therefore, the reaction rate should increase first and then decrease with VOC concentration increasing [10]. The bimolecular L–H model that takes into account the competitive adsorption of water molecules can describe a similar process [10,15,16], whereas multiple regression using this model results in multiple solutions. It is difficult to get reasonable reaction parameters from the model.

This paper focuses on several familiar VOCs (toluene, o-xylene, and benzene) in indoor air to investigate their UV-PCO degradation performance, and proposes a simple dynamic model that is applicable from low to relatively high concentration levels by considering the effect of catalyst deactivation.

2. Experiments

2.1. Experimental system

The experiments were carried out in a glass-plate reactor (Fig. 1). Compressed synthetic air (mixture of oxygen and nitrogen with volume ratio 21:79) was supplied by a compressed cylinder.

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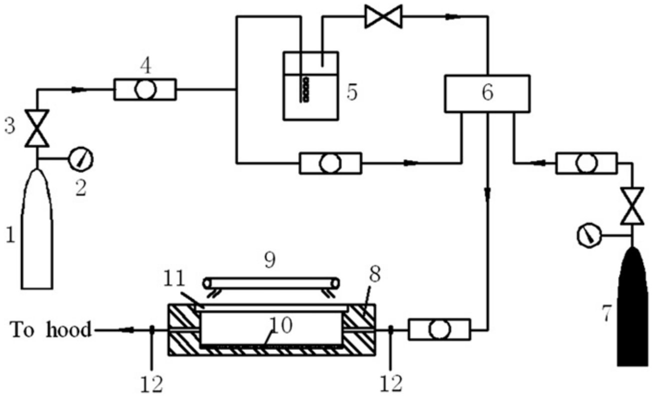

Fig. 1. Schematic of the glass-plate photoreactor (1) compressed synthetic air; (2) pressure regulator; (3) needle value; (4) mass flow controller; (5) humidifier; (6) mixing box; (7) VOC source; (8) stainless steel; (9) ultraviolet germicidal lamp; (10) TiO2-coated glass-plate; (11) quartz window; (12) sampling points.

The air passed through a mass flow controller and was then divided into two streams. One stream passed through a mass flow meter while the other passed through a humidifier. The air stream with a flow rate of 1.56 L/min mixed with the supplied VOC in the mixing box. The mixed gas was supplied through a mass flow controller to the reactor.

2.2. Experimental conditions and methods

In this study, the VOC concentration in supply air was controlled to 0–3.5 ppm for toluene, 0–2.5 ppm for o-xylene and 0–2.1 ppm for benzene. Degussa P25 TiO_2 was prepared on the clear glass plate ($152.4 \times 25.4 \times 2.0$ mm^3) using the dip-coating method [17]. The catalyst loading was 1.55 mg/cm^2, which was a bit high to ensure that the glass surface was fully covered with TiO_2. PCO reactions occur only at the catalyst surface. A germicidal lamp (254 nm peak intensity, 20 W) provided UV light for the reactor. The average UV intensity on the reaction surface was 234 μW/cm^2, measured by a UV power meter (Uncertainty is ±5%) before the PCO reaction began, and the value was assumed to remain unchanged during the experiment. The measurement was conducted by placing the UV power at the same height of the glass plate, before the plate was put in place. All experiments were performed at a room temperature of 18 ± 2 °C. The relative humidity was set to a common air conditioning level of 45 ± 5%. The air samples were collected by Tenax tubes from the inlet and outlet of the reactor under steady state (30 min–1 h was required for the experimental system to reach a steady state after the experiment started). The samples were analyzed by GC-MSD (Agilent 6850/5975 VL). To ensure that no photoactivity decay occurred due to strongly adsorbed oxidation intermediates, the catalyst was regenerated after each experiment by continuous ultraviolet illumination and flow of clean air (approximate 45% RH) through the reactor overnight [5,18].

3. Results and discussion

3.1. L–H model fitting and deficiency for toluene

Assuming that the mass transfer is not the limiting step and that the effect of intermediate products is negligible, then the unimolecular L–H model can be expressed as [7,8]:

$$r = k\frac{KC}{1+KC} \tag{1}$$

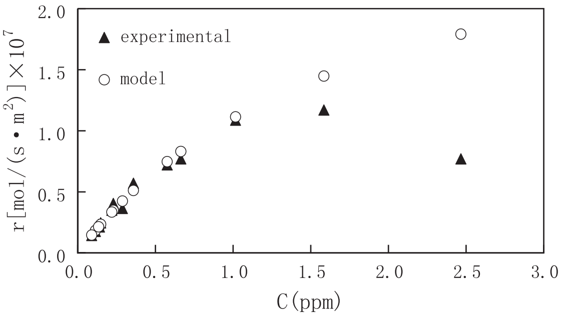

Fig. 2. Experiments vs. unimolecular L–H model for toluene.

where k is the average reaction rate constant (mol/(m^2 s)), K is the Langmuir adsorption equilibrium constant (ppm^{-1}), C is VOC concentration in the gas-phase (ppm), and r is the average reaction rate of VOC per unit catalyst coating area (mol/(m^2 s)).

It is found that the experimental results of toluene can be predicted well by the unimolecular L–H model at low levels (<1.5 ppm) (Fig. 2). The regressed values of k and K are shown in Table 1. However, the predictions significantly deviate from the experimental results at concentration levels >1.5 ppm. In particular, when the initial concentration is more than 1.5 ppm, the reaction rate of toluene will decrease, which cannot be explained by the unimolecular L–H model.

In fact, the competitive adsorption between VOC and water molecules adsorbed on the catalyst surface may not be ignored with the VOC concentration increasing. That being the case, the degradation performance of VOC should be consistent with the bimolecular L–H model at relative high concentration levels [10,15,16], namely:

$$r = k\frac{(KC)\cdot(K_{\mathrm{w}}C_{\mathrm{w}})}{(1+KC+K_{\mathrm{w}}C_{\mathrm{w}})^2} \tag{2}$$

where k is the average reaction rate constant (mol/(m^2 s)), K and K_{w} are the Langmuir adsorption equilibrium constant of the VOC and water vapor (ppm^{-1}), C and C_{w} (In these experiments, $C_{\mathrm{w}} = 8850$ ppm) are respectively the VOC and water vapor concentrations in the gas-phase (ppm), and r is the average reaction rate of the VOC per unit catalyst coating area (mol/(m^2 s)).

The parameters of k, K and K_{w} in Eq. (2) can be obtained by the multiple regressions. The optimal values of the three parameters are obviously found with multiple solutions in the regression process. Several representative groups of results are listed in Table 1:

These regression parameters (Table 1) were substituted into Eq. (2) and the predicted results of toluene are shown in Fig. 3. It can be seen that the four groups of regression parameters could all be possible solutions fitting for the experimental results. Therefore, it is difficult to get reasonable reaction parameters from the bimolecular L–H model. The reaction rate of toluene began to decline when it reached a maximum value, and the reaction rate was close

Table 1
Regression results of k, K and K_{w} for toluene.

Model	k (mol/(m^2 s))	K (ppm^{-1})	K_{w} (ppm^{-1})
Unimolecular L–H	3.119×10^{-7}	0.5468	N/A
Bimolecular L–H	7.205×10^{-7}	1.234	1.423×10^{-4}
	4.316×10^{-6}	0.6023	1.159×10^{-5}
	4.581×10^{-5}	0.5510	9.996×10^{-7}
	4.218×10^{-7}	11.47	2.312×10^{-3}