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Effect of water vapor on the by-products and decomposition rate of ppb-level toluene by photocatalytic oxidation

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ABSTRACT

It was found that there were unwanted by-products in the photocatalytic oxidation (PCO) of indoor ppb-level toluene, a typical volatile organic compound (VOC) in indoor air. However, up to now the control mechanism of the generation of the products has not been clear. In this study we address the problem: a titania-coated glass-plate reactor was applied to study the by-products and decomposition rate; the by-products generated under a series of water vapor concentrations were instantaneously identified by proton transfer reaction-mass spectrometer (PTR-MS); the results indicate that water vapor has a significant effect not only on the photocatalytic decomposition rate of toluene, but also on its by-products generation; the competitive adsorption mechanism between water vapor, toluene and its by-products was analyzed. By-products may make the typical Langmuir–Hinshelwood model unfeasible in real application. A health risk assessment of the by-products was also introduced. The results show that the maximum decomposition efficiency does not always lead to minimal by-products and lowest health risk. What it does show is that when evaluating the performance of photocatalytic air purification, health risks posed by the by-products should be the primary concern rather than the decomposition efficiency.

1. Introduction

In modern indoor environments, many materials and products emit harmful contaminants, such as toluene, benzene and formaldehyde [1–4]. These contaminants influence human health, comfort and productivity [5]. Some have been found to be associated with asthma, nasopharyngeal cancer and multiple subjective health complaints [6]. Photocatalytic oxidation (PCO) is an innovative approach to eliminating volatile organic compounds (VOCs) indoors [7,8] and has been investigated by many researchers [9–11]. The results of complete PCO for VOCs should be CO_2 and H_2O. Such a reaction seems perfect for removing VOCs from the air since both CO_2 and H_2O are nontoxic. Indoor air cleaners based on the PCO approach have been developed and are commercially available. However, recent studies [12–15] have found that the photocatalytic reactions are not as complete as they are assumed to be. The photocatalytic oxidation process sometimes stops along the way, yielding aldehydes, ketones or organic acids [16]. Some of these unwanted by-products are relatively more harmful to people's health than the original contaminants [13].

Logically, the by-product generation is influenced by the photocatalytic degradation route, which is controlled through the reaction conditions (the irradiation intensity of ultraviolet light, concentrations of pollutants and humidity, reaction temperature etc.) [17]. In previous studies, the water vapor level was found to play an extremely important role in photocatalytic oxidation. The adsorbed water molecules on the reaction surface are the main source of hydroxyl radicals $OH^\bullet$, which is the dominant strong oxidant for pollutant decomposition. It has been reported that under UV illumination, the number of hydroxyl radicals formed is directly proportional to the adsorbed water molecules [18]. However, excessive water vapor on the catalyst surface will inhibit the reaction rate because the presence of water vapor competes with pollutants for adsorption sites on the photocatalyst, thus reducing the pollutant removal rate [19–21]. Normally, the influence of water vapor on PCO reactions follows the adsorption competition relationship. With an increase of water vapor, the PCO reaction rate will initially increase before decreasing, with a maximum value in between [20].

However, there are few studies relating to the effect of water vapor on the generation of PCO by-products [15,22,23]. In this work we studied the effect of water vapor (typical indoor levels, relative humidity: 0–70%) on the PCO by-products and decomposition rate of ppb-level toluene.

2. Experimental

2.1. UV-PCO reaction setup

The experiment was carried out in a stainless steel plate-type UV-PCO reactor [13]. Two photocatalyst-coated glass plates

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(76.0 mm × 25.0 mm × 1.0 mm) were placed in the reactor. The photocatalyst powders (commercial Degussa P25, with a primary particle diameter of 300 nm, a specific surface area of 50 m^2/g, and a crystal distribution of 70% anatase and 30% rutile) were deposited on the glass plate as a film using the dip-coating method [13] with a net weight of 22 mg loading on the reaction side. Compressed air from a gas cylinder was divided into two streams. One stream passed through a mass flow controller and the other passed through a bottle-wash humidifier to control the humidity. The gas from another cylinder with 500 ppmv toluene was mixed with the compressed air and then was supplied to the plate-type PCO reactor. All the air-flow rates were controlled by two mass flow controllers. Two UV-C lamps (Philips Hg-Lamp, TUV 15W G15T8 UV-C, made in Holland) with a peak UV radiation at 254 nm were used to irradiate the reactor through a quartz glass.

2.2. PTR-MS measurement

A standard type of PTR-MS (*P*roton *T*ransfer *R*eaction-*M*ass *S*pectrometer, Ionicon Analytik, Austria) was applied to detect the gas-phase concentrations of various pollutants at sub-ppbv levels [13,16,24]. The *M*ass-*I*dentification-*D*etection (MID) mode of the PTR-MS was used during the research. MID was used to continuously trace some specific compounds identified from the mass-scan mode [13]. The temperatures of the detection chamber and the sampling tube were set to 60 °C. Toluene (m/z 93 signal) measured by the PTR-MS was calibrated by the gas chromatography–mass spectrometry method and its measurement accuracy was ±10%. For formaldehyde (m/z 31 signal), it was calibrated by the MBTH (3-methyl-2-benzothiazolinonehydrazone hydrochloride) spectrophotometry method under various water vapor levels and its measurement accuracy was ±5%. For other organic by-products, the measurement accuracy of the PTR-MS was estimated at ±25%.

2.3. Experimental conditions

All the experiments were performed at a common indoor air conditioning level with a temperature of 25.0 ± 1.0 °C, and a *r*elative *h*umidity (RH) of 3–70%. Inlet concentrations of toluene were adjusted in the range of 90–800 ppbv. The total airflow rate through the PCO reactor was kept at 0.55 l/min with a residence time of 0.2 s. The UV radiation intensity on the reaction surface was 0.43 mW/cm^2 at the wavelength of 254 nm which was measured using a UV-C power meter (HANDY 176, made in China). Firstly, the air-flow rate and inlet concentration of toluene were set. After the reactor inlet/outlet toluene concentration reached steady state, water vapor with high concentration was introduced from the inlet of reactor. When the inlet/outlet toluene and water vapor concentrations reached a steady state, the UV lamp was turned on to illuminate the reaction surface. All reported measurements were taken after the effluent pollutants concentration reached a sustained level. Secondly, an adjustment was made to reduce the inlet water vapor concentration. When the inlet toluene and water vapor reached a new steady state, the UV lamp was turned on and a new set of measurements taken. These adjustments were made 5–8 times under various inlet toluene concentrations (90–800 ppbv). All experiments at each inlet toluene concentration were repeated twice and 3 times for 400 and 800 ppbv. After each experiment, the TiO_2 films were photochemically regenerated by continuous illumination (94 mW/cm^2) and flow of humid air (RH = 60%) through the reactor overnight, in order to remove the possible, strongly adsorbed by-products.

2.4. Data analysis

The photocatalytic oxidation efficiency of toluene, ε was defined as

$$\varepsilon = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \quad (1)$$

where C_{inlet} and C_{outlet} are the inlet and outlet toluene concentrations, respectively.

The average reaction flux was obtained from the mass balance in the reactor:

$$r = \frac{G(C_{\text{inlet}} - C_{\text{outlet}})}{A} = \frac{GC_{\text{inlet}}\varepsilon}{A} \quad (2)$$

where r is the average reaction flux per surface area, G is the gas flow rate and A is the total surface area (specific surface area times the total amount of P25). In this study, A is equal to 2.2 m^2 for the photocatalyst-coated reaction films.

The carbon balance was analyzed through summing the concentration of carbon atoms from all detected compounds. The carbon balance ratio between outlet and inlet, η_{carbon}, was defined as

$$\eta_{\text{carbon}} = \frac{\sum_i C_{\text{outlet},i} \times (\text{number of carbon atoms of compound } i)}{\sum_j C_{\text{inlet},j} \times (\text{number of carbon atoms of compound } j)} \quad (3)$$

The risk assessment to human health of these by-products was introduced through a health-related index (HRI) [13]. It was:

$$\text{HRI}_i = \frac{C_i}{\text{REL}_i} \quad (4)$$

where REL_i is the recommended exposure limit of compound i. Some research institutes have published the REL values of various VOCs (Table 1), such as U.S. NIOSH (National Institute for Occupational Safety and Health). If HRIi exceeds the value 1, it indicates that the concentration of compound i is larger than its REL, that is, it will cause health risk to human being. HRI is used to quantify the effect of harmful by-products below. The HRI values of any carcinogenic compounds were summed to present the carcinogenic risk of PCO by-products:

$$\text{HRI}_{\text{car}} = \sum_i \text{HRI}_{\text{car},i} \quad (5)$$

3. Results

3.1. Effect of water vapor on the decomposition rate of toluene

Formaldehyde, methanol, propylene, acetaldehyde, benzaldehyde, etc. were found to be the main photocatalytic by-products of toluene in our previous research [13]. In the present study, the concentration changes of these compounds during the photocatalyic reaction were traced through the PTR-MS. Fig. 1 shows the changes of toluene and its main by-products versus the relative humidity, with an inlet toluene concentration of 400 ppbv. It was seen that the outlet toluene concentrations decreased when the water vapor levels were reduced from 62.1 to 16.0% (Fig. 1(a)). This indicated that the lower water vapor levels promoted the photocatalytic oxidation of toluene. However, when the water vapor level was 3.1%, the outlet concentration of toluene increased gradually until it finally almost reached the inlet concentration of toluene (Fig. 1(b)). This demonstrated that the TiO_2 film was being deactivated during the photocatlytic reaction.

Fig. 2 summarizes the photocatalytic oxidation efficiencies of toluene versus water vapor levels with the inlet toluene concentrations of 90, 145, 250, 400, 600, 700 and 800 ppbv. It shows that the profiles of toluene oxidation efficiency varied significantly with water vapor concentrations. When the inlet toluene concentrations were lower than 250 ppbv, the efficiencies always decreased