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Kinetic modeling of promotion and inhibition of temperature on photocatalytic degradation of benzene vapor

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Abstract

This study investigated the effects of temperature, humidity, and benzene concentration on the photocatalytic oxidation of benzene vapor over titanium dioxide. An annular packed-bed photocatalytic reactor was employed to determine the intrinsic oxidation rates for the photocatalysis of benzene. Degussa P-25 TiO_2 was used as the photocatalyst and a 15 W near-UV lamp (350 nm) was used as the light source. The experiments were conducted at influent benzene concentrations of 250–450 ppmv, water vapor concentrations of 13,500–27,500 ppmv, and reaction temperatures ranging from 100 to 200 °C. Benzene oxidation rates increased with temperature below 160–180 °C, but decreased with temperature above 160–180 °C. Raising the reaction temperature increased the chemical reaction rates but reduced the reactant adsorption rate on TiO_2 surfaces. The overall reaction rate increased with temperature, indicating that the reduction of reactant adsorption rate did not affect the overall reaction, and thus the chemical reaction was the rate-limiting step. As the chemical reaction rate gradually exceeds the reactant adsorption rate with temperature, the rate-limiting step was shifted from the chemical reaction to the reactant adsorption. Additionally, the competitive adsorption between benzene and water for the active sites on TiO_2 resulted in the promotion and inhibition of reaction rate by humidity. This study developed a modified bimolecular Langmuir–Hinshelwood kinetic model to simulate the temperature and humidity related promotion and inhibition of the photocatalysis of benzene. The correlation developed here was used as a basis for determining the apparent activation energy of 0.76 kcal/mol and adsorption enthalpies of benzene and water of -20.1 and -13.7 kcal/mol.

Keywords: Photocatalysis; TiO_2; Benzene; Model; Temperature; Humidity

1. Introduction

Photocatalytic oxidation process recently has attracted attention as a method for decomposing many organic pollutants. These pollutants may include light hydrocarbons [1–10], aromatics [2,3,11–26], and chlorinated compounds [27–31]. Owing to its low toxicity, high reactivity, and low cost, titanium dioxide (TiO_2) is a well-known semiconductor that has been widely used as the photocatalyst for decomposing many volatile organic compounds (VOCs). Many studies have investigated several major variables that may influence VOC degradation rates. These variables may include concentrations of oxygen and VOCs, humidity, illuminated light intensity, types or amounts of photocatalysts, reaction temperature, and even the reactor configurations. Among these variables, both humidity and reaction temperature may either promote or inhibit the photocatalytic degradation rates. However, few studies have investigated the influences of reaction temperature on the photocatalysis of VOCs. The role that reaction temperature plays in the photocatalysis of benzene remains unclear. Moreover, the special effects of humidity and reaction

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temperature on the photocatalytic reaction deserve in-depth study.

Reviewing the contribution of humidity to gas-phase photocatalytic oxidation of organic compounds in related investigations, water is reported to be able to inhibit the photocatalysis of some VOCs including trichloroethylene (TCE), perchloroethylene (PCE), acetone and ethylene [2,3,5,7,9,10,29–31]. Ibusuki and co-workers [11,23,25] indicated that the presence of water vapor could boost the photocatalytic oxidation of benzene and toluene. Moreover, Peral and Ollis [2], Obee and Brown [3,4] and Wang and Ku [26] reported that appropriate humidity could encourage photocatalysis of benzene, toluene, *m*-xylene, and formaldehyde, while excess humidity inhibited their reactions. Obee and Brown [3] demonstrated that the promotion and inhibition of photocatalysis by water vapor might result from the amount of hydroxyl groups, which are main active sites, formed on TiO_2 surfaces and the competitive adsorption between water vapor and organics on the active sites.

Few studies have examined the influence of reaction temperature on the gas-phase photocatalytic oxidation of contaminants. The photocatalytic degradations rates of ethylene, benzene and toluene were observed to generally increase with reaction temperature [5,7,12,14,17], while the photocatalytic degradation rate of TCE decreased with increasing temperature [17]. Notably, Blake and Griffin [1] showed that the photocatalytic reaction rate of 1-butanol increased with temperature from 25 to 105 °C, and then fell with further increase in temperature. The research group of Falconer found that the photocatalytic reaction rate of acetaldehyde was found to reach a peak at around 140 °C [8]. The mechanisms of the thermal promotion and inhibition of the photocatalytic reaction remains unclear, and further investigation is required.

Langmuir–Hinshelwood (L–H) reaction rate equation is a well-known reaction kinetic that is generally applied to discuss photocatalytic reactions [2,3,4,6,10,27,30,32]. Two bimolecular L–H rate equations shown below are generally applied to describe the competitive adsorption between organics and water.

$$r = k_0 \frac{K_1 C_1}{1 + K_1 C_1 + K_2 C_2} \tag{1}$$

$$r = k_0 \frac{K_1 C_1 K_2 C_2}{(1 + K_1 C_1 + K_2 C_2)^2} \tag{2}$$

where r denotes the photooxidation rate; k_0 represents the rate constant; K_1 and K_2 are Langmuir adsorption equilibrium constants, and C_1 and C_2 denote the reactant gas-phase concentrations. Obee and Hay [7] and Cao et al. [10] applied Eq. (1) to express the inhibited photocatalysis of both ethylene and 1-butene by water vapor. Eq. (1) implies that water vapor does not participate in the reaction but competes with the organics for the active sites on the TiO_2 surface. On the other hand, Obee and Brown [3,4] used Eq. (2) to express the promotion and inhibition of photocatalysis of toluene by both organic concentration and water vapor at room temperature, implying that water vapor not only competitively adsorbed on the active sites with organics, but also can react with each other.

Generally, the temperature-dependence of chemical reactions follows an Arrhenius law. For example, Fu [5] and Obee [7] described apparent activation energy of 3.3–3.8 kcal/mol for ethylene oxidation. Obee and Hay [7] further included explicit temperature-dependence in the L–H expression and yielded an enthalpy of adsorption of ethylene of around −2.6 kcal/mol. The thermal dynamic parameters, including apparent activation energy and adsorption enthalpy of various VOCs, to be widely obtained are required for understanding how temperature influences the photocatalytic degradation of VOCs.

This work investigates the influences of contaminant concentration, humidity, and especially reaction temperature on the photocatalytic oxidation of benzene. This study develops a kinetic model for interpreting the interactions among contaminant concentration, humidity, and reaction temperature on TiO_2 surfaces. The tested water vapor concentration ranged from 15,300 to 27,500 ppmv, and the reaction temperatures ranged from 100 to 200 °C. Intrinsic oxidation rates were determined as the benzene disappearance rates for influent benzene concentrations from 250 to 450 ppmv.

2. Experimental apparatus

The experimental apparatus designed for this study include a gas generation system, a photocatalytic reactor, and a sampling and analytical system as shown in Fig. 1. Artificial benzene-containing gas streams, which had been prepared by diluting benzene gas with additional nitrogen and oxygen, were used as influent gases for the photocatalytic reactor. The influent and effluent concentrations of benzene were determined using a gas chromatography (GC/FID, HP 4890 Series II plus) with a separation column of VOCOL (Supleco, 60 m × 0.53 mm). The water vapor content of the gas stream was determined with a hygrometer (Hygro M-2, General Eastern).

An annular packed-bed photocatalytic reactor with a total volume of 150 cm^3 was built by assembling two concentric pyrex glass tubes (Fig. 1). Gas streams flowed through the space between the concentric glass tubes. Three millimetre diameter glass pellets coated with about 0.20 g Degussa P-25 TiO_2 were packed in the space as the photocatalysts. The immobilized TiO_2 glass pellets were prepared by initially etching the pellets at 100 °C with a 5.0 M NaOH solution for 24 h. After being rinsed with D.I. water, the pellets were soaked in 5% Degussa P-25 TiO_2 slurry for 10 min, and then dried at room temperature. The immobilized pellets were then baked at 105 °C overnight. The photocatalyst was used in the all tests and there was no apparent poison phenomenon for the TiO_2 observed in the entire experimental of this study. A 15W fluorescent black light lamp (F10TBLB, GE) was used as the light source to activate TiO_2. The black light lamp