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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

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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

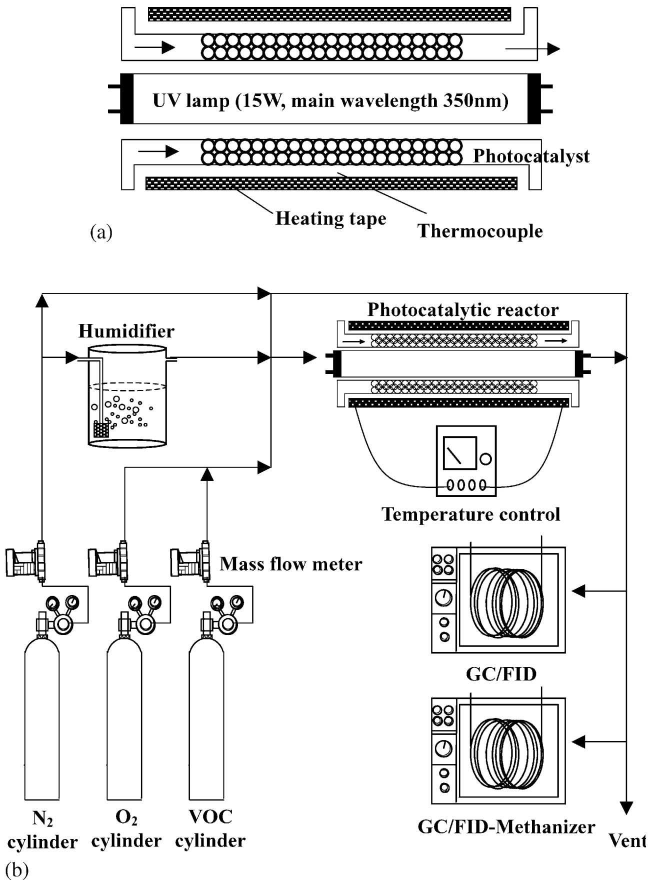

Fig. 1. The schematic diagram of the experimental set up: (a) photocatalytic reactor and (b) photocatalytic reaction system.

had a maximal spectrum wavelength of 350 nm. The photocatalytic reactor was wrapped with heating tape to adjust reaction temperature.

Several experiments with continuous declines in temperature from 200 to 100 °C were performed to investigate the influence of reaction temperature on the photocatalytic oxidation of benzene. The reaction temperature was maintained for at least 2 h in each run to collect experimental data in a steady state. The experiments were repeated to make sure that the results can be reproducible and the TiO_2 was not poison. The tested temperatures were 200, 180, 160, 140, 120 and 100 °C. Several experimental parameters included influent benzene concentrations (250–450 ppmv), water vapor concentrations (15,300–27,500 ppmv), oxygen content of 20%, and a reaction time of 8.0 s at 100 °C. The contents of both the influent and the effluent gas streams of photocatalytic reactors were analyzed. The reaction rate of benzene is defined as follows.

$$r = \frac{C_{\text{in}} - C_{\text{out}}}{t} \tag{3}$$

where r is the oxidation rate of benzene (ppmv/s); C_{in} and C_{out} are the inlet and outlet benzene concentrations (ppmv); t is the retention time that gas stream pass thought the packed-bed of the reactor (s).

3. Results and discussion

3.1. Effect of temperature

Fig. 2 plots the reaction rates of benzene versus reaction temperature by irradiating with or without near-UV light. Benzene did not degrade at reaction temperatures below 200 °C in the dark (without irradiation by near-UV light). On the contrary, rapid decomposition of benzene was clearly observed in light (with irradiation by near-UV light). The reaction rates of benzene increased as the reaction temperature increased from 100 to 160 °C, then decreased from 160 to 240 °C, and, finally increased again above 240 °C. Comparing the reaction rates of benzene in both dark and light, the decomposition of benzene resulted mainly from the pure photocatalytic reaction at temperature below 200 °C, and the combined effect of the thermocatalytic and photocatalytic reaction occurred at temperature above 200 °C. This study examined the behavior of the pure photocatalytic reaction of benzene, and the reaction temperature is limited to the range of 100–200 °C in subsequent experiments.

Figs. 3 and 4 illustrate how temperature affects the photocatalytic reaction rates of benzene under various influent benzene and water vapor concentrations, respectively. The reaction rates of benzene peaked at a reaction temperature of roughly 160–180 °C. Similar results have been reported by other investigators for the photocatalytic oxidation of 1-butanol and acetaldehyde [1,8]. According to the gas-solid catalytic theory, surface reaction includes three steps: reactant adsorption, chemical reaction, and product desorption. Increasing the reaction temperature not only increases the chemical reaction rate and product desorption rate, but also reduces the reactant adsorption rate [33]. The increase of

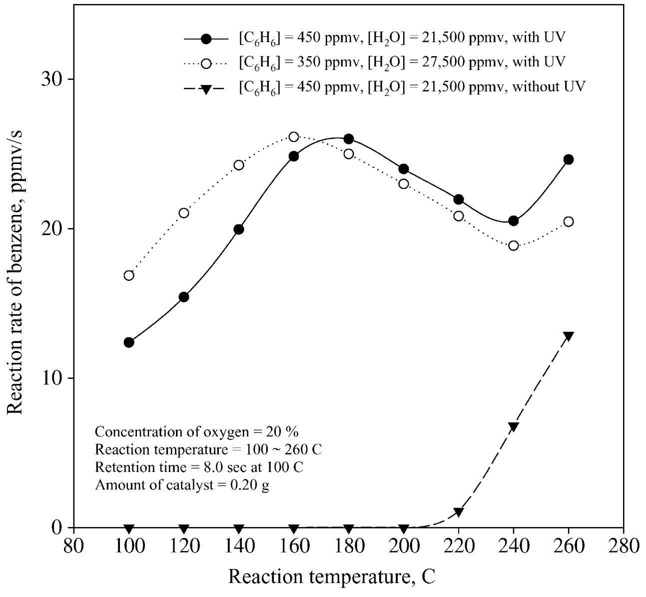

Fig. 2. The effect of temperature on the reaction rate of benzene with or without near-UV light.

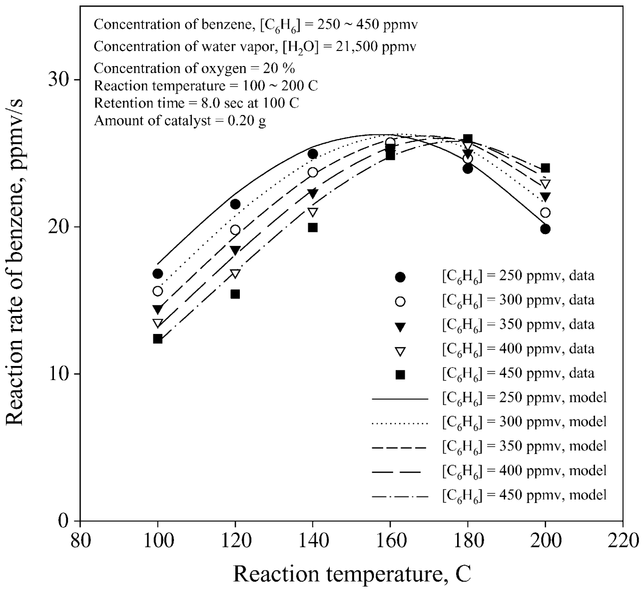

Fig. 3. The effect of temperature on the reaction rate of benzene for various influent benzene concentrations.

chemical reaction rate and product desorption rate cause the increase of reaction rate. Correspondingly, the decrease of reactant adsorption rate decreases the reaction rate. The slowest step is the rate-limiting step. In this work, the benzene reaction rate increased with increasing temperature, revealing that the reduction of reactant adsorption rate did not affect the overall reaction. Meanwhile, the chemical reaction or product desorption was the slowest step in the reaction, even if they increased with temperature. Consequently, chemical reaction or product desorption was the rate-limiting step of photocatalytic reaction below 160–180 °C. With the chemical reaction rate or the product desorption rate increasing continuously and the reactant adsorption rate decreasing with increasing temperature, the chemical reaction rate or the product desorption rate gradually exceeded the reactant adsorption rate, which gradually became the slowest rate step. Thus, the rate-limiting step shifted from the chemical reaction or the product desorption to the reactant adsorption.

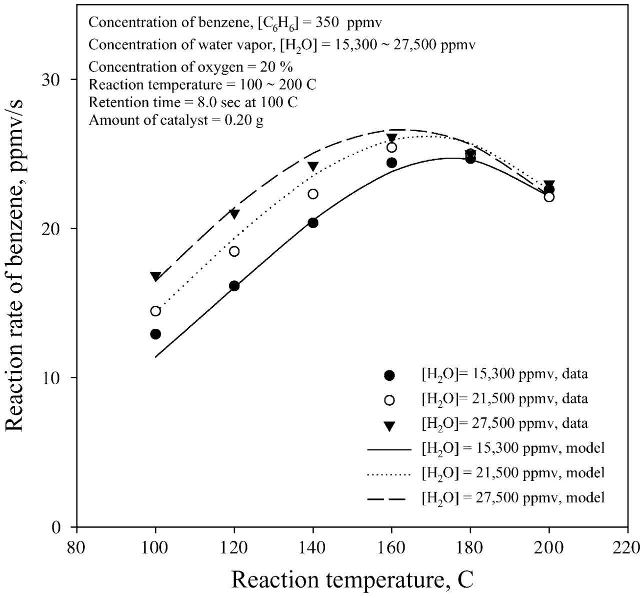

Fig. 4. The effect of temperature on the reaction rate of benzene for various water vapor concentrations.

3.2. *Effect of influent benzene concentration and water vapor*

Fig. 5a shows the effect of influent benzene concentration on the reaction rate of benzene for 100–160 °C. The reaction rate of benzene decreased with increasing influent benzene concentration for four temperatures. Fig. 5c shows the effect of water vapor on the reaction rate for 100–160 °C given a constant benzene concentration. The reaction rates increased with increasing water vapor concentration. From these two plots, competition adsorption clearly was observed among benzene and water on the active sites at temperatures of 100–160 °C.

Based on active-site theory and consider a dual-site reaction: a molecule of A on a site reacts with a molecule of B on a neighboring site to product C. If reactant adsorption is rate controlling, an increase in concentration of A and B will result in an increase in rate of reaction. Support product desorption control, no increase in rate with a rise in concentration of A and B. When the chemical reaction control, if A is in excess on the surface, increasing B concentration or decreasing A concentration will both allow more B molecules on the surface and therefore increase the reaction rate. Increasing A concentration will swamp the surface with A, crowding out B and further decreasing the reaction rate [34]. The relative adsorption affinity of A and B influence the adsorption ability of A and B on TiO_2 surface [7]. Accordingly, the reaction mechanism of photocatalytic oxidation of benzene was a dual-site reaction of benzene and water was observed in Fig. 5a and c; in addition, the chemical reaction, not products desorption and reactant adsorption was the rate-limiting step at temperature range from 100–160 °C. The reaction equation of photocatalytic oxidation of benzene was suggested as follows [19,23]:

$$TiO_2 + h\nu \rightarrow h^+ + e^- \qquad (4)$$

$$C_6H_6 + H_2O_{(ad)} + h^+ \rightarrow \ldots \rightarrow \text{Products} \qquad (5)$$

Notably, the reaction rates of benzene decreased with increasing influent benzene concentration in Fig. 5a, indicating that the relative adsorption affinity of benzene on TiO_2 is higher than that of water.

As temperature rise to 180 and 200° C, the reaction rates increased with increasing benzene concentration in Fig. 5b. The reaction rate did not decrease clearly with increasing water vapor concentration in Fig. 5d. This result demonstrated that the reactant adsorption rapidly reduced with rising temperature. The rate-limiting step was shifted from the chemical reaction to the adsorption of benzene above 180 °C. Besides,

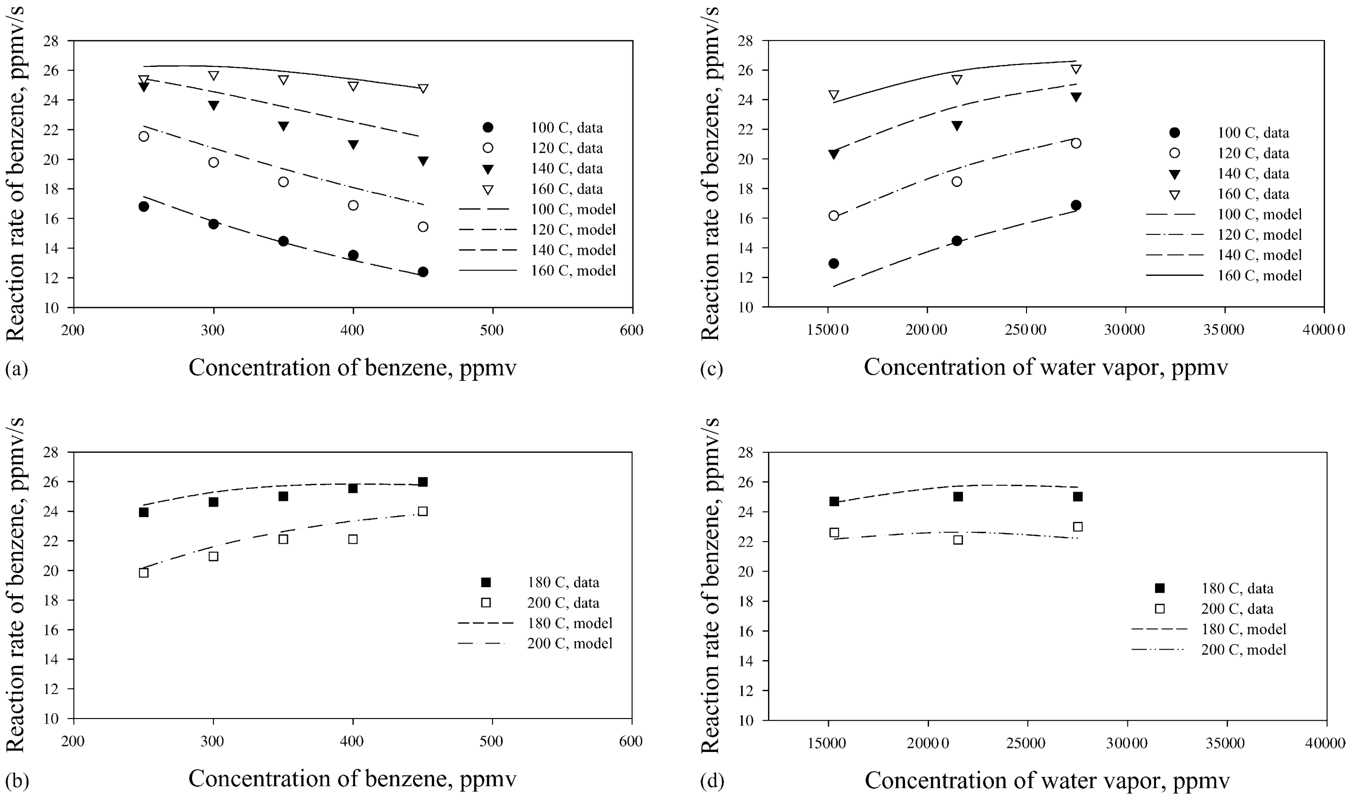

Fig. 5. The effects of influent benzene concentration and humidity at 100–200 °C. (a) and (b) the reaction rate vs. influent benzene concentration. (H_2O = 21,500 ppmv, O_2 = 20%, retention time = 8.0 s at 100 °C, amount of catalyst = 0.20 g; (c) and (d) the reaction rate vs. water vapor concentration. (C_6H_6 = 350 ppmv, O_2 = 20%, retention time = 8.0 s at 100 °C, amount of catalyst = 0.20 g.

the reaction rates decreased with increasing temperature at temperatures of 180–200 °C, indicating that the utility of the active sites decreased with rising temperature.

Generally, adsorption affinity reduces with increasing temperature, and the higher adsorption affinity of reactant to be influent by temperature was exceeded the lower one. Accordingly, the adsorption affinity of benzene decreased more than that of water with increasing temperature [7]. This theory can explain why the slopes of Fig. 5a and c are gradually approach zero with increasing temperature. Based on the above description, the difference in adsorption affinity of benzene and water reduces with increasing temperature. This result causes the coverage of benzene and water on TiO_2 gradually approach. Therefore, the effect of influent benzene concentration and water vapor both reach a plateau.

3.3. Kinetic model

For simulating the competition adsorption reaction among benzene and water on TiO_2, a bimolecular Langmuir–Hinshelwood (L–H) model was applied to describe the behavior of photocatalytic degradation of benzene. Several assumptions were made: (1) benzene and water are adsorbed on separate sites and without dissociation; (2) benzene and water react with each other, and (3) reaction products, carbon dioxide, carbon monoxide and intermediates do not influence the observed oxidation rates, and the influence of any intermediates was neglected.

$$r = k_{\mathrm{LH}} \frac{K_{\mathrm{B}} C_{\mathrm{B}} K_{\mathrm{W}} C_{\mathrm{W}}}{(1 + K_{\mathrm{B}} C_{\mathrm{B}} + K_{\mathrm{W}} C_{\mathrm{W}})^2} \tag{6}$$

where k_{LH} denotes the rate constant (ppmv/s); K_{B} and K_{W} represent the Langmuir adsorption equilibrium constants of benzene and water vapor (ppmv^{-1}), respectively, and C_{B} and C_{W} are the gas-phase concentrations of benzene and water vapor, respectively (ppmv).

Table 1 lists the reaction rate constants and adsorption equilibrium constants of the modified bimolecular L–H model at various reaction temperatures. k_{LH} increased with reaction temperature. Meanwhile, both K_{B} and K_{W} decreased with increasing reaction temperature. Obee and

Table 1
The reaction rate constants and adsorption equilibrium constants of modified bimolecular Langmuir–Hinshelwood model for various reaction temperature for Eq. (6)

Temperatures (°C)	k_{LH} (ppmv/s)	K_{B} (ppmv $^{-1}$)	K_{W} (ppmv $^{-1}$)
100	97	2.5	0.0090
120	100	0.82	0.0045
140	103	0.25	0.0020
160	107	0.0781	0.00106
180	115	0.0199	0.00037
200	121	0.0080	0.00016

Table 2
The reaction rate constants and adsorption equilibrium constants of modified bimolecular Langmuir–Hinshelwood model for Eq. (9)

Parameters	Units	Value
k_{LH}'	ppmv/sec	270.4
K_B'	$ppmv^{-1}$	9.81×10^{-11}
K_W'	$ppmv^{-1}$	2.06×10^{-9}
E	kcal/mol	0.76
ΔH_B	kcal/mol	−20.1
ΔH_W	kcal/mol	−13.7

Hay [7] reported similar results for the oxidation kinetics of ethylene. Generally, the rate constant follows an Arrhenius temperature-dependence and increase exponentially with temperature [33]. The adsorption of all species on the surface is exothermic, therefore the higher temperature, the smaller the adsorption equilibrium constant [33,35]. The rate constant and the adsorption equilibrium constant is expressed as follows [7,33,35]:

$$k_{LH} = k_{LH}' \exp\left(\frac{-E}{RT}\right) \tag{7}$$

$$K = K' \frac{\exp(-\Delta H/RT)}{\sqrt{T}} \tag{8}$$

where k_{LH}' denotes the (temperature-independence) rate constant (ppmv/s); E represents an apparent activation energy (kcal/mol); T is the reaction temperature (K); R is the gas constant (1.99×10^{-3} kcal/mol K); K' denotes the (temperature-independence) adsorption equilibrium constant, and ΔH represents the change of enthalpy of reactant. Therefore, Eqs. (7) and (8) can then be substituted into Eq. (6) to simulate the temperature-dependence of the modified L–H model, and the apparent activation energy of reaction and the enthalpy of benzene and water can be determined.

Accordingly, the temperature-dependence reaction rate is presented as follows:

$$r = k_{LH}' \exp\left(\frac{-E}{RT}\right) \times \frac{K_B'[\exp(-\Delta H_B/RT)/\sqrt{T}]\, C_B K_W'[\exp(-\Delta H_E/RT)/\sqrt{T}]C_W}{(1 + K_B'[\exp(-\Delta H_B/RT)/\sqrt{T}]\, C_B + K_W'[\exp(-\Delta H_E/RT)/\sqrt{T}]C_W)^2} \tag{9}$$

where K_B' and K_W' denote the (temperature- independent) Langmuir adsorption equilibrium constants ($ppmv^{-1}$), and ΔH_B and ΔH_W represent the changes in enthalpy that accompany the adsorption of benzene and water, respectively (kcal/mol). Least-square optimization was applied to determine the values of the unknown constants in Eq. (9). Fig. 6 shows the regression result, while Table 2 lists the correlation constants, apparent activation energy, and enthalpy of reactants. The values of E, ΔH_B and ΔH_W were 0.76, −20.1 and −13.7 kcal/mol, respectively.

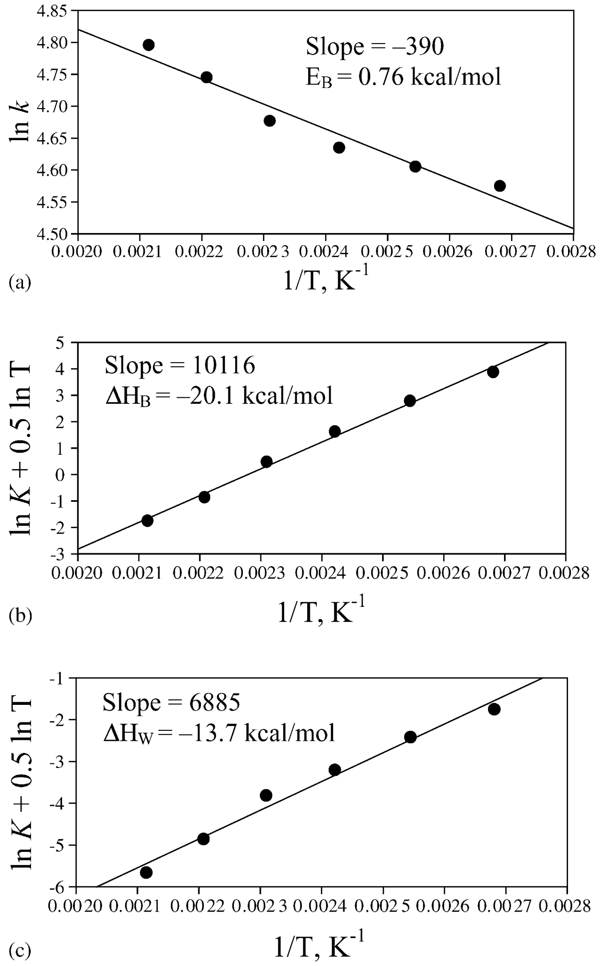

Fig. 6. ln k or ln K + 0.5 ln T vs. inverse temperature. (a) Apparent activation energy of benzene (E), (b) enthalpy of benzene (ΔH_B) and (c) enthalpy of water (ΔH_W).

A value of −13.7 kcal/mol for the enthalpy of adsorption of water on TiO_2 approaches the adsorption energy of physisorbed water on TiO_2, −12.2 kcal/mol [36]. This result indicated that the interaction of water on TiO_2 surface belongs to physisorption. On the other hand, due to benzene being observed to be stronger adsorbed on the TiO_2 surface than is water in this work, a value of −20.1 kcal/mol for the enthalpy of adsorption of benzene is reasonable.

Figs. 3, 4 and 5 compare the simulated result (lines in figures) of this modified L–H model and the experimental data (symbols in figures). The modified L–H kinetic model can explain both the promotion and inhibition of the reaction by temperature at 100–200 °C for various benzene concentrations in Figs. 3 and 4. The simulated results further confirmed that raising the temperature increased the chemical reaction rate but inhibited the reactant adsorption by model simulation. Additionally, the effect of influent benzene concentration and humidity at reaction temperatures of 100–200 °C was also successfully simulated by this model in Fig. 5.

Three experiments are conducted in this study to assess if the above model can be applied under other experimental

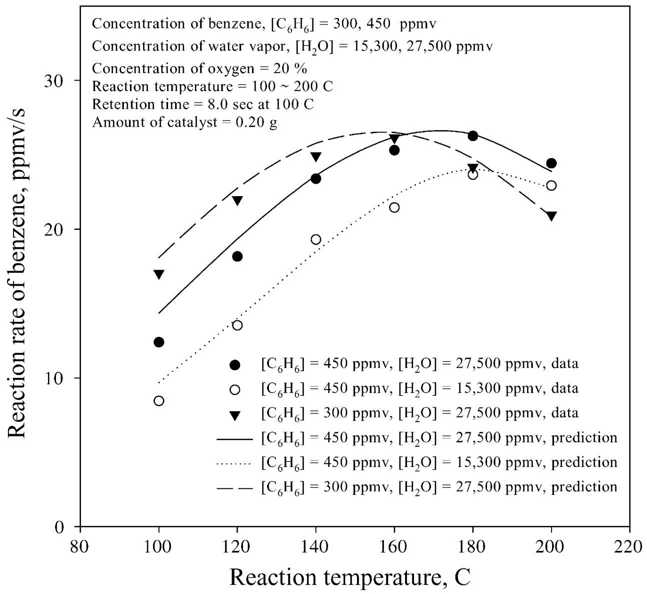

Fig. 7. The model prediction results of the reaction rate of benzene vs. reaction temperatures for various influent benzene concentrations and humidity.

condition. Fig. 7 showed that the predicted curves by model coincided with the experimental data. The model result appeared suitable for predicting the reaction rate in other condition.

4. Conclusion

The proposed bimolecule L–H kinetic model accurately simulated the promotion and inhibition of the photocatalytic oxidation of benzene by temperature, as well as the competition adsorption between benzene and water on the TiO_2 surface. The competitive adsorption between benzene and water on active sites caused the promoted or inhibited reaction by humidity. k_{LH} increased while K_B and K_W decreased with increasing temperature, confirming that increased reaction temperature could enhance the chemical reaction rate, but reduced the adsorption rates of benzene and water. When the chemical reaction rate exceeds the reactant adsorption rate, the rate-limiting step shifted from chemical reaction to reactant adsorption on the TiO_2 surface with increasing temperature. The benzene adsorption enthalpy of −20.1 kcal/mol and water adsorption enthalpy of −13.7 kcal/mol indicated that the relative adsorption affinity of benzene on TiO_2 exceeded that of water. However, the combined effect of thermocatalytic and photocatalytic of benzene was observed as the temperature exceeded 200 °C. This topic is worth investigating further in the future.

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