



# Photocatalytic oxidation of heptane in the gas-phase over TiO<sub>2</sub>

Jing Shang<sup>\*</sup>, Yaoguo Du, Zili Xu

*Department of Environmental Science and Engineering, Jilin University, Changchun 130023, People's Republic of China*

Received 24 October 2000; received in revised form 26 March 2001; accepted 26 March 2001

## Abstract

In this paper, gas-phase photocatalytic oxidation (PCO) of heptane over UV-illuminated TiO<sub>2</sub> was carried out at ambient temperature in a batch reactor. Complete oxidation of heptane with almost stoichiometric production of CO<sub>2</sub> and H<sub>2</sub>O was observed. The intermediates detected were propanal, butanal, 3-heptanone, 4-heptanone and carbon monoxide. A scheme of the possible mechanism for PCO of heptane over TiO<sub>2</sub> was suggested. Langmuir–Hinshelwood kinetics equation was obtained from the results at different initial concentrations of heptane, oxygen, moisture and light intensity. The photocatalytic activity of TiO<sub>2</sub> can be sustained indefinitely. This can be attributed to the production of water in the system, which can replenish the consumed hydroxyl radicals. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Photocatalytic oxidation mechanism; Reactive oxygen species; Reaction kinetics; Photocatalytic activity

## 1. Introduction

Volatile organic compounds (VOCs) are an important class of air pollutants, which are considered together with nitrogen oxides, sulfur oxides and particulates as the most important anthropogenic pollutants generated in urban and industrial areas (Avila et al., 1998). The term VOCs is used to identify all compounds containing carbon and present in the atmosphere, with the exception of elemental carbon, carbon monoxide and carbon dioxide (Augugliaro et al., 1999). VOCs have drawn considerable attention in the last decade. Among the methods to oxidize VOCs, heterogeneous photocatalytic oxidation (PCO) is one of the most attractive, due to the mild experimental conditions under which the runs are usually carried out. Photocatalysis has been largely used for photooxidation of many organic molecules in liquid-phase (Hustert and Zepp,

1992; Yan et al., 1994; Herrmann, 1999; Assabane et al., 2000). Simultaneously, photocatalysis in gas-phase has been attracting more and more attention (Obee and Brown, 1995; Avila et al., 1998; Augugliaro et al., 1999). As we know, alkanes, such as heptane, are among VOCs in the air. Therefore, the studies on the gas-phase PCO of alkanes become important.

Djaghri et al. (1974) once reported photoinduced oxidation of C<sub>2</sub>–C<sub>8</sub> alkanes on TiO<sub>2</sub> at ambient temperature. In general, they observed that alkanes (C<sub>n</sub>H<sub>2n+2</sub>) formed ketones (C<sub>n</sub>H<sub>2n</sub>O) and other aldehydes (C<sub>m</sub>H<sub>2m</sub>O) with 2 < m < n. If the alkane was branched, the ketone was C<sub>m</sub>H<sub>2m</sub>O with 3 < m < n. The reactivity of different types of carbon atoms followed the sequence: C<sub>tert</sub> > C<sub>quat</sub> > C<sub>sec</sub> > C<sub>prim</sub>. The carbon atom, which is preferentially attacked by oxygen, is the one which presents the highest electron density together with the least steric obstruction, but any of the carbon atoms of the alkane molecule may be attacked. A proposed mechanism for the oxidation of alkanes led to the formation of an alcohol intermediate which in turn oxidized to an aldehyde or ketone. The neutral atomic oxygen, O, is

<sup>\*</sup> Corresponding author. Fax: +86-431-8923907.

E-mail address: dashanshang@yahoo.com.cn (J. Shang).

reactive species to form alcohols from alkanes. This O species is assumed to be formed by the reaction between adsorbed oxygen species such as  $O_2^-$  and positive hole. ESR measurements have detected the existence of  $O_2^-$  in the presence of molecular oxygen on irradiated  $TiO_2$  sample (Gravelle et al., 1971), and it is then quite possible that  $O_2^-$  is able to combine with positive holes to form free or trapped, neutral or ionic atomic oxygen species (Bickley et al., 1973). Herrmann et al. (1979) stated that reactive oxygen species such as O and  $O_2^-$  played important roles in the PCO of isobutane. The mechanism suggested involved O attack of isobutane to form activated intermediate, which was then transferred to final products (acetone,  $CO_2$  and  $H_2O$ ) by the aid of  $O_2$ .

The PCO of simple light alkanes ( $<C_3$ ), especially methane, into oxygen containing chemicals has also attracted much attention (Gratzel et al., 1989; Suzuki et al., 1990; Wada et al., 1993). For example, Wada et al. (1993) investigated the PCO of simple  $C_1$ – $C_3$  alkanes at temperatures from ambient to ca. 550 K. They observed that the PCO of methane produced a small amount of methanal together with carbon dioxide, and the PCO of ethane produced ethanal. The reaction with propane gave propanal and acetone. The yields of the products were very small at ambient temperature, and increased with increasing temperature up to 550 K. The species involving adsorbed oxygen must be partially responsible for deep oxidation of alkanes or intermediates to carbon dioxide. They assumed that the PCO of light alkanes consists of two steps: the former step is the reaction between photogenerated reactive oxygen species and alkanes, and the latter includes thermochemical conversion of intermediates to the final products and desorption of the products from the catalyst bed.

Most researchers proceeding with the gas-phase PCO of alkanes are primarily interested in partial oxidation, and the oxidation mechanisms have been focused on. However, few studies have been carried out on either reaction kinetics or the activity of photocatalyst. In this paper, we present a study of the gas-phase PCO of heptane at ambient temperature over UV-illuminated  $TiO_2$  powder. Complete PCO of heptane was observed, and the oxidation mechanism, reaction kinetics, as well as photocatalytic activity of the catalyst were investigated.

## 2. Experimental

### 2.1. Preparation of the $TiO_2$ photocatalyst

The nanocrystalline  $TiO_2$  catalyst used in this study was prepared by the method of alkoxide hydrolysis. Ethanol was slowly added to 20 ml  $TiCl_4$  to form  $Ti(OC_2H_5)_4$  and the produced HCl smoke was adsorbed

by NaOH solution. The resultant solution was refluxed until the color of the solution changed from yellow to white. Then 5 ml deionized water was added and the white precipitate was washed by ethanol. After drying, the substrate was calcinated at 573 K. X-ray analysis (D/Max- $\gamma$ A powder diffractometer with nickel filtered  $CuK\alpha$  source) of the  $TiO_2$  particle revealed the presence of anatase only and the mean crystallite size was estimated to be 12 nm using the Scherrer equation (Ogawa and Abe, 1981). The specific surface area of the  $TiO_2$  particle was  $60.5\text{ m}^2/\text{g}$ , as determined by BET method (Micromeritics ASAP 2010).

### 2.2. Photocatalytic reaction

The light source used in this investigation was a 20-cm-long 400 W UV lamp. The primary wavelength distribution of this lamp is at 365 nm and the light intensity is  $5.3\text{ mW}/\text{cm}^2$  at 15 cm away from the lamp. During the experimental period, the light intensity could be varied by changing the distance between the lamp and the reactor. The batch reactor used was a 300 ml cylindrical quartz tube. In the experiment, 0.1 g of  $TiO_2$  particles was spread uniformly over the internal surface of the reactor. After this, the reactor was vacuum-packed and suitable amounts of heptane, oxygen and moisture were injected into the reactor through a sample port. Then ultrapurity nitrogen was mixed with the reactants in the reactor to one atmospheric pressure. When adsorption reached equilibrium, as measured by gas chromatograph (GC), the reaction was then started by turning on the lamp. Subsequently, the content of heptane in the reactor, obtained by a gastight syringe from the sample port, was measured every 15 min by a Varian 3700 GC equipped with a flame ionization detector and an SE-54 quart capillary column at 323 K. The measurement of  $O_2$  was performed by a GC equipped with a thermal conductivity detector (TCD) and a molecular sieve stainless column at 323 K. The contents of  $CO$ ,  $CO_2$  and  $H_2O$  were determined by GC (TCD) using molecular sieve (323 K), GDX-303 (323 K) and GDX-401 (383 K) column, respectively. The gas-phase intermediates produced in the system were analyzed by a HP 6890 GC/HP 5973 MS and were identified by comparison to the National Institute of Standards (NIST) mass spectra library.

## 3. Results and discussion

### 3.1. The products of PCO of heptane

The PCO of heptane did not proceed in the absence of either  $TiO_2$  or UV light irradiation. However, when the gas mixture containing heptane (0.4%, v/v, i.e.,

16.6 g/m<sup>3</sup>) and oxygen (20%, v/v) entered the photo-reactor with 0.1 g UV-illuminated TiO<sub>2</sub>, the PCO of heptane occurred. There were propanal, butanal, 3-heptanone, 4-heptanone, CO, CO<sub>2</sub> and H<sub>2</sub>O formed during the PCO of heptane. Because the production of butanal and 4-heptanone was little, we selected propanal, 3-heptanone and CO as intermediates to follow the variations of their concentrations. Fig. 1 shows the variations of concentrations of heptane and by-products including CO<sub>2</sub>, H<sub>2</sub>O, propanal, 3-heptanone and CO under irradiation time. From Fig. 1, we can see that the concentration of heptane decreased with the irradiation time. The concentrations of CO<sub>2</sub> and H<sub>2</sub>O increased with increasing irradiation time and changed little when heptane oxidized completely. Propanal and 3-heptanone reached their maximum concentrations after 30 and 60 min of irradiation, respectively, and then decayed. CO built up almost to its maximum yield while heptane oxidized completely, and then degraded gradually. About 99.7% of stoichiometric CO<sub>2</sub> and H<sub>2</sub>O had been formed after 360 min of irradiation.

### 3.2. Mechanism aspects

From the results illustrated above, we know that the PCO of heptane led to the formation of intermediates such as aldehydes and ketones, and finally CO<sub>2</sub> and H<sub>2</sub>O were produced. The PCO process of heptane can be written as

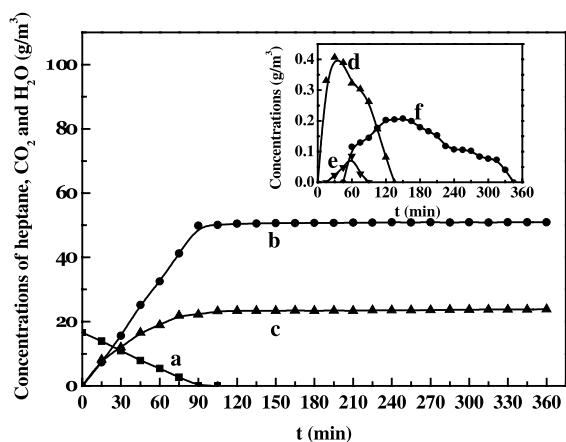
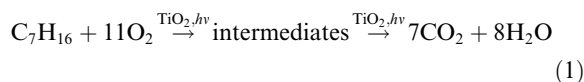
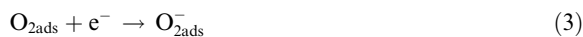


Fig. 1. Degradation of heptane (a), evolution of CO<sub>2</sub> (b) and H<sub>2</sub>O (c), and formation and decay of propanal (d), 3-heptanone (e) and CO (f) under irradiation (d, e and f were depicted in inset). Heptane concentration = 16.6 g/m<sup>3</sup>, O<sub>2</sub> = 20% (v/v), without water, UV = 5.3 mW/cm<sup>2</sup>.

Taking into account the photocatalytic properties of *n*-semiconductor TiO<sub>2</sub>, the initial reaction steps on UV-illuminated TiO<sub>2</sub> can be summarized in the following scheme (subscript ads represent adsorption):

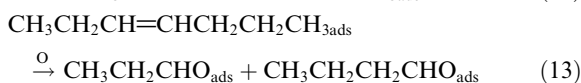
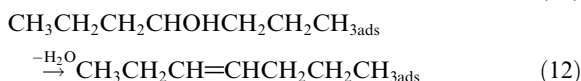
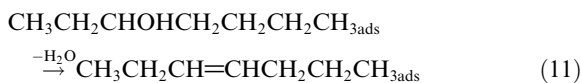
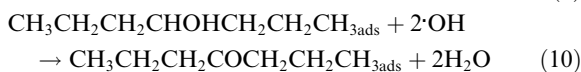
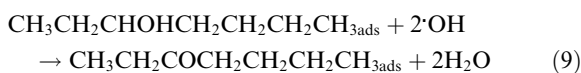


When a photon with energy of  $h\nu$  matches or exceeds the band-gap energy,  $E_g$ , of TiO<sub>2</sub>, the conduction-band electrons ( $e^-$ ) and valence-band holes ( $h^+$ ) generate on the surface of TiO<sub>2</sub>. In the absence of the electron and hole scavengers, most of them recombine with each other within a few nanoseconds. If the scavengers or surface defects are present to trap the electrons or holes,  $e^-$ - $h^+$  recombination can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced (Park et al., 1999). In this case, oxygen adsorbed on the surface of TiO<sub>2</sub> plays a significant role in the reaction with electrons, with O<sub>2</sub><sup>-</sup>, O and O<sup>-</sup> being the products of this electron transfer (reactions (3)–(5)) (Peral and Ollis, 1992). At the same time, photogenerated holes are trapped by hydroxyl ions or water on the surface, producing hydroxyl radicals (reactions (6) and (7)), which play important roles in photocatalytic reactions (Park et al., 1999). Moreover, reactions among O<sub>2</sub><sup>-</sup>, O and H<sub>2</sub>O<sub>ads</sub> give rise to the formation of  $\cdot\text{OH}$  and HO<sub>2</sub><sub>ads</sub><sup>·</sup> and HO<sub>2</sub><sub>ads</sub><sup>·</sup> is another source of  $\cdot\text{OH}$  (Pellizzetti and Minero, 1993; Augugliaro et al., 1999). In the gas phase, organic substrates can themselves act as adsorbed traps for the photogenerated holes (reaction ((8)), since water molecules are not the predominant species in contact with the catalyst in the gas phase. Although in the presence of water vapor,  $\cdot\text{OH}$  groups are present on the TiO<sub>2</sub> surface and their contribution to photooxidation cannot be discarded, the preliminary adsorption of organic compounds is a very important prerequisite for highly efficient detoxification (Fox and Dulay, 1993). In fact, in a photocatalytic reaction, TiO<sub>2</sub> photogenerated valence-band holes (+3.1 V vs NHE at pH 0) are capable of oxidizing any organic compound (Alberici and Jardim, 1997).

No alcohol was detected in the present experiment, but it was shown previously (Djeghri et al., 1974; Djeghri and Teichner, 1980) that the first step of the PCO of alkanes was the formation of this intermediate whose dehydration or oxidation proceeded generally with a higher rate than its formation from alkanes. In

this case, reactive oxygen species such as O or O<sup>-</sup> can attack C<sub>7</sub>H<sub>16ads</sub> or C<sub>7</sub>H<sub>16ads</sub><sup>+</sup> to form C<sub>7</sub>H<sub>15</sub>OH<sub>ads</sub>.

The production of 3-heptanone and 4-heptanone indicates the formation of 3-heptanol and 4-heptanol, which can be attacked by hydroxyl radicals to produce corresponding heptanone and H<sub>2</sub>O (reactions (9) and (10)). 3-heptanol or 4-heptanol can also proceed with the dehydration reaction to form 3-heptene, which can be further oxidized to propanal and butanal (reactions (11)–(13)). The mechanism suggested here is consistent with that of Blake and Griffin (1988), which involved the hydroxyl radicals attack of 1-butanol to give butanal and water, or a dehydration leading to the formation of 1-butene and water. It has also been observed that when the corresponding alcohols and alkenes are photooxidized as reactants, the same ketones and aldehydes are produced (Djehri and Teichner, 1980).



The resulting aldehydes and ketones can be oxidized to acids under the function of ·OH and O<sub>2</sub> (Soyan and Murasawa, 1994). CO<sub>2</sub> can then be derived from further photodecarboxylation. The photodecarboxylation of carboxylic acid in the presence of TiO<sub>2</sub> powder in gas-phase regime is well known (Sato, 1983; Augugliaro et al., 1986; Muggli and Falconer, 1999). The mechanism involved ·OH radical attack, and also the direct discharge of carboxylate ions by photogenerated holes should also be taken into account. As for CO, reactive oxygen species such as O<sup>-</sup>, O and O<sub>2</sub><sup>-</sup> have been suggested as the adsorbed species responsible for the PCO of CO to form CO<sub>2</sub> (Sato and Kadowaki, 1987; Linsbigler et al., 1996; Dickinson et al., 1999).

### 3.3. Kinetics of the PCO of heptane

Langmuir–Hinshelwood (L–H) rate expression has been widely used in liquid-phase photocatalysis and has been found of utility in gas-phase photocatalysis (Peral and Ollis, 1992; Alberici and Jardim, 1997; Vorontsov et al., 1999). If the concentrations of oxygen and water remain constant, this equation can be simplified as

$$r = \frac{kKC}{1 + KC}, \quad (14)$$

where  $r$  is the reaction rate (g/m<sup>3</sup> min),  $C$  is the concentration of reactant (g/m<sup>3</sup>),  $k$  is the rate constant (g/m<sup>3</sup> min), and  $K$  is the adsorption constant (m<sup>3</sup>/g). Inverse of the equation gives

$$\frac{1}{r} = \frac{1}{kKC} + \frac{1}{k}. \quad (15)$$

If the assumed L–H form is valid, then a plot of  $1/r$  vs  $1/C$  should be linear.

Fig. 2 shows under the condition of a fixed oxygen content of 20% (v/v), i.e., 265.6 g/m<sup>3</sup>, and without water, the variation of inverse of reaction rates ( $1/r$ ) under inverse of heptane concentrations ( $1/C_h$ ). From Fig. 2, we can see that the experimental data are in good agreement with this L–H rate form. Fig. 3 shows the variation of inverse of reaction rates ( $1/r$ ) of 16.6 g/m<sup>3</sup> heptane under different inverse of oxygen concentrations ( $1/C_{O_2}$ ). The linear plot indicates that the kinetics of oxygen also fits the L–H form. Fig. 4 shows the variation of inverse of reaction rates ( $1/r$ ) of 16.6 g/m<sup>3</sup> heptane under different concentrations of water ( $C_w$ ) ranging from 3.7 to 22.4 g/m<sup>3</sup>. The linear plot of  $1/r$  with  $C_w$  indicates that water in the gas feed inhibits the heptane oxidation rate. Widely differing rate influences of water have been reported for different gas-phase photocatalytic oxidation reactions. Dibble and Raupp (1990) found the rate of TCE oxidation to be zero-order in water for H<sub>2</sub>O mole fractions below 10<sup>-3</sup> and to become strongly inhibitory with a -3-order rate dependence for water mole fractions between 5 × 10<sup>-3</sup> and 5 × 10<sup>-2</sup>. In contrast, Ibusuki and Takeuchi (1986) found that the PCO rate of trace toluene in air was

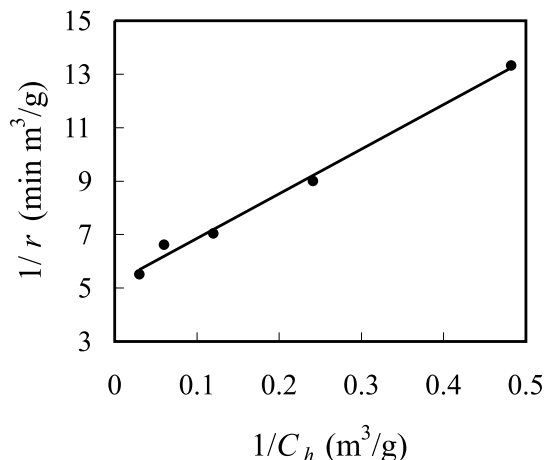


Fig. 2. The variation of inverse of reaction rates under different inverse of heptane concentrations. O<sub>2</sub> = 20% (v/v), without water, UV = 5.3 mW/cm<sup>2</sup>.

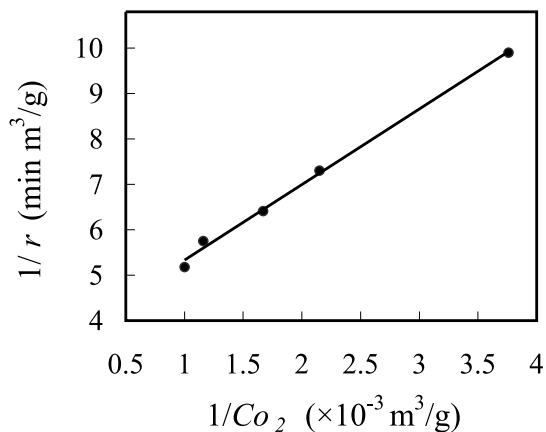


Fig. 3. The variation of inverse of reaction rates under different inverse of oxygen concentrations. Heptane concentration = 16.6 g/m<sup>3</sup>, without water, UV = 5.3 mW/cm<sup>2</sup>.

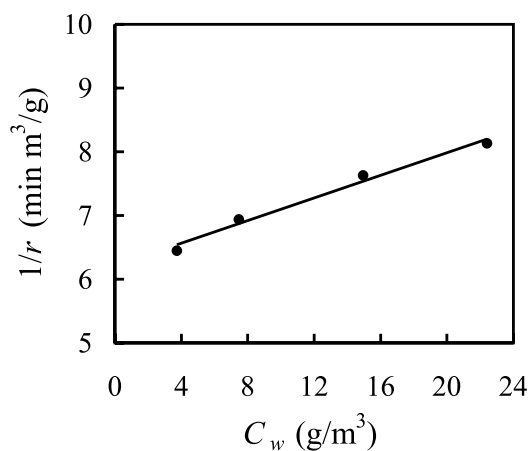


Fig. 4. The variation of inverse of reaction rates under different water concentrations. Heptane concentration = 16.6 g/m<sup>3</sup>, O<sub>2</sub> = 20% (v/v), UV = 5.3 mW/cm<sup>2</sup>.

enhanced by water vapor, increasing almost linearly with water vapor content between 0% and 60% relative humidity. In the present study, water vapor concentrations of 3.7–22.4 g/m<sup>3</sup> are clearly inhibitory for heptane photooxidation. The inhibitive effect of water can be explained as (Peral and Ollis, 1992; Wang et al., 1998): (1) there is a competition for adsorption between heptane and water vapor; (2) water vapor molecules may block heptane adsorption sites and (3) the increased content of water vapor can destroy the equilibrium between consumption (due to the consumption of hydroxyl free radicals) and adsorption of water (to replenish the hydroxyl free radicals) to keep stable reaction rate, with more adsorption of water vapor mole-

cules on the surface of catalyst to lower the reaction rate.

From the analyses of Figs. 2–4 above, we can assume the following L–H rate form, which describes reaction rate concentration dependences:

$$r = k \left( \frac{K_h C_h}{1 + K_h C_h + K_w C_w} \right) \left( \frac{K_{O_2} C_{O_2}}{1 + K_{O_2} C_{O_2}} \right). \quad (16)$$

Values of  $k = 0.315 \text{ g}/\text{m}^3 \text{ min}$ ,  $K_h = 0.295 \text{ m}^3/\text{g}$ ,  $K_w = 0.098 \text{ m}^3/\text{g}$  and  $K_{O_2} = 0.0024 \text{ m}^3/\text{g}$  were then calculated from Figs. 2–4. From the L–H rate expression of heptane PCO described above, we can see that the adsorptions of heptane and oxygen were on different types of sites and there were competitive adsorptions between heptane and water vapor for the same site, assuming that the major parameters were concentrations of heptane, oxygen and the introduced water and no influence of reaction products on reaction rate.

The reaction rate constant is a function of the light intensity with the following relationship (Peral and Ollis, 1992):

$$k = k_0 I^\alpha, \quad (17)$$

where  $k_0$  is the rate constant independent of light intensity,  $\text{g}/(\text{m}^3 \text{ min}(\text{mW}/\text{cm}^2)^\alpha)$ ,  $I$  is the light intensity,  $\text{mW}/\text{cm}^2$ , and  $\alpha$  is the order constant. By substituting the above relationship to the expression of (16) under fixed initial concentrations of heptane, oxygen and humidity, the rate expression should be

$$r = k' I^\alpha, \quad (18)$$

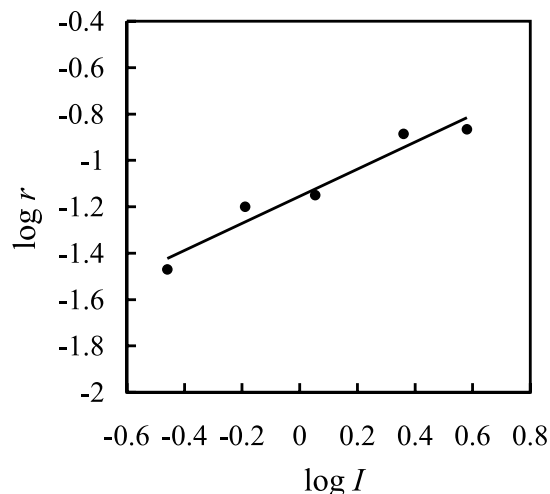


Fig. 5. The linear regression of  $\log r$  vs  $\log I$ . Heptane concentration = 4.15 g/m<sup>3</sup>, O<sub>2</sub> = 20% (v/v), without water.

where

$$k' = k_0 \left( \frac{K_h C_h}{1 + K_h C_h + K_w C_w} \right) \left( \frac{K_{O_2} C_{O_2}}{1 + K_{O_2} C_{O_2}} \right). \quad (19)$$

Fig. 5 shows the plot of  $\log r$  vs  $\log I$ . A straight line with slope  $\alpha = 0.58$  and intercept  $\log k' = -1.154$ . Since  $C_h$ ,  $C_w$ ,  $C_{O_2}$ ,  $K_h$ ,  $K_w$  and  $K_{O_2}$  are known, rate constant  $k_0$  can be determined. The value of  $\alpha = 0.58$  indicated that the electron–hole pairs are consumed more rapidly by recombination than by chemical reactions (Wang et al., 1998).

### 3.4. Photocatalyst activity

When the same  $TiO_2$  catalyst was used consecutively over 100 runs (i.e., over 200 h), the photoactivity of it is the same as that of fresh one, i.e., the photoactivity of  $TiO_2$  can be sustained indefinitely. It has been reported by others that the catalytic activity of  $TiO_2$  could be maintained indefinitely under an abundance of water vapor (Dibble and Raupp, 1990; Peral and Ollis, 1992; Obee and Brown, 1995; Alberici and Jardim, 1997). It is well established that UV illumination of hydroxylated titania in the presence of gaseous  $O_2$  produces surface hydroxyl radicals. Infrared spectroscopy studies (Phillips and Raupp, 1992) during TCE oxidation show that the titania surface becomes partially dehydroxylated as the reaction proceeds. If hydroxyl radicals are consumed in the heterogeneous oxidation reactions, then the surface must be continuously rehydrated if long-term catalytic activity is to be maintained. As can be seen from Fig. 1, the adsorbed heptane and intermediates were photo-oxidized quickly to final products  $CO_2$  and  $H_2O$ , therefore the surface of  $TiO_2$  is clean after each run of photoreaction. In addition, although hydroxyl radicals may sustain continuous consumption during photocatalysis, water formed as a product of the reaction may replenish the consumed hydroxyl radicals through rehydration to maintain photocatalyst activity.

## 4. Conclusions

The conversion of 99.7% was obtained during the PCO of heptane with propanal, butanal, 3-heptatone, 4-heptatone and CO being the intermediates, which can be further photooxidized to the final products  $CO_2$  and  $H_2O$ . Reactive oxygen species such as  $O_2^-$ ,  $O^-$ ,  $O$  and  $\cdot OH$  play important roles in the PCO of heptane. The reaction rate could be successfully written by L–H kinetic form. In addition, the photocatalytic activity of  $TiO_2$  can be sustained indefinitely due to the formation of water as the product, which can replenish the consumed hydroxyl radicals.

## Acknowledgements

This work was supported by the National Science Foundation of China.

## References

- Alberici, R.M., Jardim, W.F., 1997. Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide. *Appl. Catal. B Environ.* 14 (1), 55–68.
- Assabane, A., Ichou, Y.A., Tahiri, H., Guillard, C., Herrmann, J.M., 2000. Photocatalytic degradation of polycarboxylic benzoic acids in UV-irradiated aqueous suspensions of titania. Identification of intermediates and reaction pathway of the photomineralization of trimellitic acid (1,2,4-benzene tricarboxylic acid). *Appl. Catal. B: Environ.* 24 (1), 71–87.
- Augugliaro, V., Palmisano, L., Schiavello, M., Sclafani, A., 1986. Photodecomposition of adsorbed ethanoic acid over silica gel catalyst in a flow system. *J. Catal.* 99 (1), 62–71.
- Augugliaro, V., Voluccia, S., Loddo, V., Marchese, L., Martra, G., Palmisano, L., Schiavello, M., 1999. Photocatalytic oxidation of gaseous toluene on anatase  $TiO_2$  catalyst: mechanistic aspects and FT-IR investigation. *Appl. Catal. B: Environ.* 20 (1), 15–27.
- Avila, P., Bahamonde, A., Blanco, J., Sanchez, B., Cardona, A.I., Romero, M., 1998. Gas-phase photo-assisted mineralization of volatile organic compounds by monolithic titania catalysts. *Appl. Catal. B: Environ.* 17 (1–2), 75–88.
- Bickley, R.I., Munuera, G., Stone, F.S., 1973. Photoadsorption and photocatalysis at rutile surface II photocatalytic oxidation of isopropanol. *J. Catal.* 31 (3), 398–407.
- Blake, N.R., Griffin, G.L., 1988. Selectivity control during the photoassisted oxidation of 1-butanol on titanium dioxide. *J. Phys. Chem.* 92 (20), 5697–5701.
- Dibble, L.A., Raupp, G.B., 1990. Kinetics of the gas–solid heterogeneous photocatalytic oxidation of trichloroethylene by near UV illuminated titanium dioxide. *Catal. Lett.* 4, 345–354.
- Dickinson, A., James, D., Perkins, N., Cassidy, T., Bowker, M., 1999. The photocatalytic reforming of methanol. *J. Mol. Catal.* 146 (1/2), 211–221.
- Djaghri, N., Formenti, M., Juillet, F., Teichner, S.J., 1974. Photointeraction on the surface of titanium dioxide between oxygen and alkanes. *Faraday. Discuss. Chem. Soc.* 58, 185–193.
- Djaghri, N., Teichner, S.J., 1980. Heterogeneous photocatalysis: the photooxidation of 2-methylbutane. *J. Catal.* 62 (1), 99–106.
- Fox, M.A., Dulay, M.T., 1993. Heterogeneous photocatalysis. *Chem. Rev.* 93 (1), 341–357.
- Gratzel, M., Thampi, K.R., Kiwi, J., 1989. Methane oxidation at room temperature and atmospheric pressure activated by light via polytungstate dispersed on titania. *J. Phys. Chem.* 93 (10), 4128–4132.
- Gravelle, P.C., Juillet, F., Meriaudeau, P., Teichner, S.J., 1971. Surface reactivity of reduced titanium dioxide. *Disc. Faraday. Soc.* 52, 140–148.

- Herrmann, J.M., Disdier, J., Mozzanega, M.-N., Pichat, P., 1979. Heterogeneous photocatalysis: in situ photoconductivity of study of TiO<sub>2</sub> during oxidation of isobutane into acetone. *J. Catal.* 60 (3), 369–377.
- Herrmann, J.M., 1999. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today* 53 (1), 115–129.
- Hustert, K., Zepp, R.G., 1992. Photocatalytic degradation of selected azo dyes. *Chemosphere* 24 (3), 335–342.
- Ibusuki, T., Takeuchi, K., 1986. Toluene oxidation on UV-irradiated titanium dioxide with and without O<sub>2</sub>, NO<sub>2</sub> or H<sub>2</sub>O at ambient temperature. *Atmos. Environ.* 20 (9), 1711–1715.
- Linsebigler, A., Lu, G.Q., Yates, J.T., 1996. CO photooxidation on TiO<sub>2</sub> (110). *J. Phys. Chem.* 100 (16), 6631–6636.
- Muggli, D.S., Falconer, J.L., 1999. Parallel pathways for photocatalytic decomposition of acetic acid on TiO<sub>2</sub>. *J. Catal.* 187 (1), 230–237.
- Obee, T.N., Brown, R.T., 1995. TiO<sub>2</sub> photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1,3-butadiene. *Environ. Sci. Technol.* 29 (5), 1223–1231.
- Ogawa, H., Abe, A., 1981. Preparation of tin oxide films from ultrafine particles. *J. Electrochem. Soc.* 128 (3), 685–689.
- Park, D.R., Zhang, J.L., Ikeue, K., Yamashita, H., Anpo, M., 1999. Photocatalytic oxidation of ethylene to CO<sub>2</sub> and H<sub>2</sub>O on ultrafine powdered TiO<sub>2</sub> photocatalysts in the presence of O<sub>2</sub> and H<sub>2</sub>O. *J. Catal.* 185 (1), 114–119.
- Pellizzetti, E., Minero, C., 1993. Mechanism of the photo-oxidative degradation of organic pollutants over TiO<sub>2</sub> particles. *Electrochim. Acta* 38 (1), 47–55.
- Peral, J., Ollis, D.F., 1992. Heterogeneous photocatalytic oxidation of gas-phase organics for air purification: acetone, 1-butanol, butyraldehyde, formaldehyde and *m*-xylene oxidation. *J. Catal.* 136 (2), 554–565.
- Phillips, L.A., Raupp, G.B., 1992. Infrared spectroscopic investigation of gas–solid heterogeneous photocatalytic oxidation of trichloroethylene. *J. Mol. Catal.* 77 (3), 297–311.
- Sato, S., 1983. Photo-Kolbe reaction at gas–solid interfaces. *J. Phys. Chem.* 87 (18), 3531–3537.
- Sato, S., Kadowaki, T., 1987. Photocatalytic activities of metal oxide semiconductors for oxygen isotope exchange and oxidation reactions. *J. Catal.* 106 (1), 295–300.
- Sopyan, I., Murasawa, S., 1994. Highly efficient TiO<sub>2</sub> film photocatalyst degradation of gaseous acetaldehyde. *Chem. Lett.* 4, 723–726.
- Suzuki, T., Wada, K., Shima, M., Watanabe, Y., 1990. Photoinduced partial oxidation of methane into formaldehyde on silica-supported molybdena. *J. Chem. Soc., Chem. Commun.* 15, 1059–1060.
- Vorontsov, A.V., Kurkin, E.N., Savinor, E.N., 1999. Study of TiO<sub>2</sub> deactivation during gaseous acetone photocatalytic oxidation. *J. Catal.* 186 (2), 318–324.
- Wada, K., Yoshida, K., Takatani, T., Watanabe, Y., 1993. Selective photo-oxidation of light alkanes using solid metal oxide semiconductors. *Appl. Catal. A: General* 99 (1), 21–36.
- Wang, L.H., Tsai, H.H., Hsieh, Y.H., 1998. The kinetics of photocatalytic degradation of trichloroethylene in gas phase over TiO<sub>2</sub> supported on glass bead. *Appl. Catal. B: Environ.* 17 (4), 313–320.
- Yan, Q., Sivils, L.D., Palepu, S.D., Kapila, S., 1994. Effects of co-contaminants on photodegradation of octachlorodibenzo-*p*-dioxin (OCDD). *Chemosphere* 29 (9–11), 2183–2192.