Kinetics of gas-phase photooxidation of p-xylene on nano TiO₂ P25 thin film

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Received 24 September 2018
Accepted for publication 29 October 2018
Published 20 November 2018

Abstract

In this investigation, the thin film of TiO₂ degussa P25 was obtained by dip coating method and calcined at 450 °C for 2h (P25-450-2) and used as photocatalyst for gas-phase photooxidation of p-xylene. The physico-chemical properties of calcined P25-450-2 powder was studied by the methods of BET adsorption, XRD, FTIR, UV–vis, Raman spectroscopies, SEM, TEM, carbon dioxide temperature-programmed desorption (CO₂-TPD). The thickness of the film was determined on the Alpha Step IQ KLA—Ctencor equipment and the point of zero charge (PZC) of the sample was determined by salt addition method. P25-450-2, having a band gap of 3.155 eV, is advisable to use UV lamps in photocatalytic reactions. The kinetics of gas-phase photooxidation of p-xylene reaction on the thin films of P25-450-2 under UV illumination was studied using a gradientless flow circulating system at atmospheric pressure and 40 °C. The obtained results showed that the kinetics of the given reaction should be written by fractional equations describing the dependence of the reaction rate on the concentration of adsorbed molecules of p-xylene and oxygen, dissociative adsorbed water vapor, and also on the total intensity of light. The reaction was proposed to follow the Langmuir-Hinshelwood mechanism.

Keywords: nano TiO₂-P25 thin film, kinetics, gas-phase photooxidation, p-xylene

Classification numbers: 2.03, 4.02, 5.07

1. Introduction

Photocatalytic oxidation (PCO) is increasingly playing an important role in environmental science. PCO is considered to be a heterogeneous catalytic reaction with individuality due to the it’s activation by light, and studies in this field focus on: (i) find new semiconductor catalysts working better in a more diverse light region; (ii) study to clarify the behavioral characteristics of the reaction.

Until now, TiO₂ have been evaluated as the most effective catalysts in ultraviolet light [1, 2]. Studies [1–3] showed that the photocatalytic activity of TiO₂ was highest at an appropriate anatase/rutile ratio. This is because the energy of valence band of the anatase and rutile phases is approximately the same, but the energy of conduction band of anatase is higher than that of rutile phase 0.3 eV. Thus, the electrons from the conduction band of anatase phase can jump to the one of rutile that limiting the rate of recombining electrons and holes. According to Bickley et al [4] the anatase/rutile structure of TiO₂ P25 promotes charge-pair separation and inhibits recombination. Ohno et al [5] found that TiO₂ P25 with 75% anatase phase showed higher photocatalytic activity than 100% anatase catalysts (ST01, ST21) and 100% rutile free TiO₂ (PT101). So far, TiO₂ P25 is considered as the most effective bare TiO₂ catalyst for the photocatalytic reaction under UV light.

In general, the analysis of the data in the references shows that for the gas-phase PCO there is a small amount of kinetic studies [6], and although there are various proposed kinetic models, most authors agreed that the photooxidation process is
a heterogeneous reaction occurring on surface of the catalysts between the adsorbed substance with oxygen in adsorption state (Langmuir-Hinshelwood model), from volume phase (Eley-Rideal model), or lattice O of TiO₂ (Mars–Van Krevelen model). Kinetic models of the propane photo-oxidation over a vanadium-doped TiO₂ catalyst were studied in a fixed-bed reactor, using 4 g of catalyst, under ultraviolet light irradiation are summarized in [7]. These models include three main mechanisms: Langmuir-Hinshelwood (LH), Eley-Rideal (ER) and Mars-Van Krevelen (MVK). According to the LH mechanism, the surface reaction between adsorbed-competing propane and oxygen was considered as the rate-determining step and common kinetic equation was accepted as follows:

\[ r = \frac{kK_{O_2}^nK_{R}^mP_{O_2}^nP_{R}^r}{(1 + K_{O_2}^mP_{O_2}^o + K_{R}P_R)^h} \]  

where \( k \) is reaction rate constant; \( K_{O_2} \) and \( K_{R} \) are adsorption equilibrium constant of oxygen and organic substrate, respectively, and \( P_i \) is their partial pressure; \( n, m \) are the orders of corresponding reactant, and \( h \) is surface coverage.

According to the Eley-Rideal mechanism, chemically adsorbed oxygen reacts with propane from the gas phase and the reaction kinetics is described by the following common equation:

\[ r = \frac{kK_{O_2}^nK_{R}^mP_{O_2}^nP_{R}^r}{(1 + K_{O_2}^mP_{O_2}^o + K_{R}P_R)^h}. \]

The Mars–Van Krevelen (MVK) mechanism has a reduction stage, in which two oxidation reactions with single or two oxidized surface sites and a stage of re-oxidation of the reducing centers on the surface by oxygen from gas phase and the kinetic equation receives the following common form:

\[ r = \frac{aK_{O_2}K_{R}^mP_{O_2}^nP_{R}^r}{(bK_{O_2}^mP_{O_2}^o + cK_{R}P_R)^h}, \]

where \( a, b, c \) are the kinetic constants; and \( n, m, l \) are the order of corresponding reactants.

For most heterogeneous catalytic reactions the Langmuir model is widely accepted [8–11]. Many authors showed that the Langmuir-Hinshelwood model is suitable for the reactions of gas-phase photocatalytic oxidation of organic compounds [12], acetone [13], methyl tert-butyl ether (MTBE) [14, 15] and the kinetic equation has the form

\[ \frac{dC}{dt} = k\theta = k \frac{KC}{1 + KC}, \]

where \( K \) is adsorption equilibrium constant of the reactant, and \( C \) is concentration of the reactant at time of observation. In paper [16], the photocatalytic activity of a TiO₂ thin film in degradation of gaseous methanol and toluene under the UV light irradiation in accordance with the LH kinetic model.

For the effect of photon flux, it was found that the reaction rate \( (r) \) depends on the photon flux of UV light \( (\Phi) \) in a power law [17]

\[ r = r'\Phi^\beta, \]

where \( r' \) is the reaction rate independent of the photon flux, and \( \beta \) is the order of photon flux.

According to authors [17–19] the order of photon flux \( (\beta) \) in equation (5) depends on the light intensity and the wavelength light, the first-order was observed when the illumination intensity is noticeably lower than 1000 – 2000 µW × cm⁻², and the half-order at the photon flux above 1000 – 2000 µW × cm⁻². In the photo-oxidation of methanol and toluene it has been found that depending on wavelength of the UV light the order of \( \Phi \) is 0.42 and 0.57 respectively under the irradiation of germicidal lamps \( (\lambda = 254\text{ nm}) \) or is 0.89 and 0.95 respectively under the irradiation of black light lamps \( (\lambda = 352\text{ nm}) \) [17]. However, Jaime et al [13] reported that the dependence of the reaction rate of the photocatalytic process on the photon intensity was not detected.

The aim of this work is to evaluate the photocatalytic activity and stability of thin film TiO₂ degussa P25, calcined at 450 °C for 2 h, for gas-phase photooxidation of p-xylene under UV illumination and to clarify the kinetics of the reaction.

2. Experimental

The TiO₂ P25 film on pyrex glass tube was obtained by submerged coating from a suspension of TiO₂ P25 according to the procedure described in detail in our previous publication [20]. The catalyst tubes were calcined at 450 °C for 2 h and catalyst is denoted by P25-450-2. Supports for the active phase of the catalysts were closed pyrex glass tubes with 19 mm in diameter, 270 mm in length and treated with aqueous hydrofluoric acid solution.

The physico-chemical properties of P25-450-2 powder catalysts were characterized by methods of Brunauer-Emmett-Teller (BET) adsorption using BET Nova 2200E equipment; x-ray diffraction (XRD) on a D8 Advance Bruker powder diffractometer; Fourier-transform infrared (FTIR) spectroscopy using Tensor 27-Bruker; scanning electron microscope (SEM) on FE-SEM JEOL 7401 and transmission electron microscope (TEM) on JEM 1400 (Jeol USA); Raman by using Labram-HR with a thermal conductivity detector. The thickness of the film was not detected.

The kinetics of the gas-phase photooxidation of p-xylene was carried out in a gradientless flow circulating system at atmospheric pressure and 40 °C. The reaction was carried out using 15 mg of thin film catalyst having illuminated area of 65 cm². Three UV lamps \( (\lambda = 365\text{ nm}) \) with the power of 8
3. Results and discussion

3.1. The properties and the activity of photocatalyst

The effect of calcination temperature on the physico-chemical properties of TiO₂ P25 catalyst was investigated in [20]. From the results it follows that calcination has led to changes in physico-chemical properties of the samples that affect the activity of the catalysts. The sample calcined at 450 °C was characterized by biggest specific surface area, as a result, it exhibited relatively high photocatalytic activity in the illumination of ultraviolet light. Inheriting the results of the publication [20] and in order to increase the catalytic properties of calcined membrane preparation, in this study, the TiO₂ P25 film after dipping, drying, was heated at 450 °C for a shorter time, of 2 h instead of 4 h as indicated in [20].

XRD pattern of P25-450-2 sample (figure 1) exhibits diffraction peaks of the anatase (2θ = 25.2°, 37.8°, 47.9°, 53.9°, 54.9°, 62.65°, 68.9°) and rutile phase (2θ = 27.4°, 35.95°, 41.2°, 56.6°) [22]. The acuteness of peaks in XRD pattern demonstrates high crystallinity of sample. According to the XRD patterns of the catalyst, the ratio of anatase to rutile in obtained catalyst was found at 80.9/19.1. This phase ratio of P25-450-2 sample causes the synergetic effect (40% ≤ [anatase] ≤ 80%) [23]. Hence, it is predicted high photoactivity to degrade organic pollutants. The average size of the P25-450-2 crystallallites was estimated approximately 21 nm by using Scherrer formula at 2θ = 25.3° [24].

On the Raman spectrum of P25-450-2 sample (figure 2) the characteristic peaks of anatase TiO₂ at 142 cm⁻¹, 394 cm⁻¹, 513 cm⁻¹, 633 cm⁻¹ and of rutile phase at 443 and 609 cm⁻¹ were observed. Furthermore, intensity of characteristic Raman peak for rutile is much lower than that for anatase. This is accordant with dominance of anatase phase as calculating phase content from the XRD result.

According to isothermal adsorption results, the BET specific surface area of P25-450-2 sample is 49.6 m² / g⁻¹ approximately (table 1). It is close to the results of the sample P25-450-4 in investigation [20].

According to the SEM image (figure 3), P25-450-2 catalyst is suggested having pseudo spherical in shape. In addition, its distribution is nearly uniform. TEM image (figure 4) indicates the co-existence of both bright and dark fields, typically for the presence of anatase and rutile phase in structure of P25-450-2 catalyst [25]. From the SEM and TEM images, the average size of the primary particles estimates about 20–30 nm. This is a good agreement with the results calculated from the XRD pattern (21 nm).

As can be seen from UV spectrum in figure 5, P25-450-2 mainly absorbs UV irradiation. Band gap energy of P25-450-2 sample based on Tauc curve (figure 6) was determined at 3.155 eV. The absorbable wavelength of the sample can be calculated by the equation λ = hc/Eg and equal 393 nm. Hence, to initiate photochemical effects in semiconductor P25-450-2, UV light was required.

As can be seen from figure 7, strong peaks in FTIR spectrum are observed at 3419, 1632, and 650 cm⁻¹. The broad peak at 3419 and the peak at 1632 cm⁻¹ are believed corresponding to the hydroxyl groups and surface-adsorbed water respectively, while the main peak at from 400 to 700 cm⁻¹ is ascribed to Ti-O stretching and Ti-O-Ti bridging stretching modes. The existence of this OH-groups explains the generation of OH• on the catalyst surface.

So, compared to P25-450-4 sample in article [20], P25-450-2 catalyst used in this study exhibited a smaller crystal size and slightly lower band gap energy. This may due to considerably shorter calcination duration was used in this study (2 versus 4 h).

CO₂-TPD pattern in the figure 8 exhibited the CO₂ desorption peaks in temperature range of 100 °C–350 °C. According to Wang et al [26] the CO₂ desorption peaks in temperature-programmed desorption (TPD) pattern of CeO₂ at temperatures of 150 °C–200 °C and above 400 °C represents the weak, medium and strong basic sites, respectively. Then, the received results showed that on P25-450-2 catalyst exist the weak and medium basic sites, moreover weak basic sites dominate. Duffy [27] reported that the basicity of TiO₂ is much greater than that of SiO₂ and is nearly the same as the basicity of CaO. Bergman [28] determined the optical basicity of TiO₂ is 0.55.

Figure 9 showed a uniform distribution of TiO₂ particles on the film and the thin film P25-450-2 has an average thickness of 2.75 µm.

From the mentioned above results, it follows that the TiO₂-P25 powder after calcination at 450 °C for 2h predominantly consist of spherical shape crystals, having an anatase/rutile phase ratio of 80/9/19.1 and band gap energy (Eg) of 3.155 eV, absorbing UV light, are capable to use UV lamps in photocatalytic reactions. This catalyst exhibited relatively high activity and stability under the illumination of ultraviolet light (figure 10). This meets the requirements for studying the kinetics of the reaction. The enhancing photoactivity of P25-450-2 sample is explained by synergetic effect of the mixture anatase and rutile phase of suitable ratio [23] and the contact of two phases makes slowly electron-hole recombination [4]. In addition, the smaller size and lower band gap energy also contributed to increased activity of P25-450-2 catalyst.

The high stability of P25-450-2 catalyst is explained by its high basicity (as shown from the CO₂-TPD result) and the small particle size, yielding less favorable conditions to coke deposit on the catalyst surface. Furthermore, the point of zero charge of P25-450-2 catalyst was determined at ~ 6.3, so in the gas-phase reaction medium its surface charge is neutral, the absence of electrostatic force causes the minimum of the interplay between surface particles and contaminants. This also contributes to reducing coke deposit on the catalyst.
surfaces. Indeed, the by-products formed on surface of P25-450-2 catalyst during photocatalytic oxidation of \( p \)-xylene were analyzed from the solution extracted in the dark from the catalyst layer in methanol after a long period of operation (several days) was estimated less than 1 mg g\(^{-1} \) catalyst. The results of the analysis (figures 11 and 12) showed that the compounds, depositing on the catalyst surface are products of the partial oxidation such as 2-methylbenzaldehyde and phthalic anhydride. They are oxygenate compounds with a low C: H ratio (CH0.5 for phthalic anhydride and CH for methylbenzaldehyde), easily combusted in reaction conditions, leading to the low amount of deposited products, that increased the stability of catalyst.

The analysis of the experimental data during the course of reaction showed that under the given conditions the catalytic activity did not change with time. Thus, all the experimental data can be used in kinetic calculations. Furthermore, the advantage of thin film catalyst is included in high efficiency and ease of recovery. The catalyst can be regenerated by treatment in air flow at 450 °C in 2 h.

3.2. Reaction kinetics

According to the results obtained above, the thin films of P25-450-2 catalyst should be considered as typical catalyst for \( p \)-xylene photooxidation in UV light. Therefore, the kinetics of reaction (6) was studied on P25-450-2 catalyst at conditions of ultraviolet irradiation.

\[
p = C_9H_{10} + 10.5O_2 \rightarrow 8CO_2 + 5H_2O. \tag{6}
\]

In the kinetic experiments the values of gas hourly space velocity on a volume basis (GHSV) varied from 26.10\(^3\) to 468.10\(^3\) h\(^{-1} \) and a catalyst film with the thickness of 2.75 – 2.90 \( \mu \)m was used. Under such conditions the influences of external as well as internal diffusions can be avoided. Indeed, in this range of flow rate the conversion extent decreased with increasing flow velocity, which indicates that there is no effect of external diffusion. The values of initial partial pressure of \( p \)-xylene \( (P_{\text{xyl}}^0) \), oxygen \( (P_{\text{O}_2}^0) \) and water vapor \( (P_{\text{H}_2\text{O}}^0) \) varied in ranges: 2.1–11.3 hPa, 105–473 hPa, and 6–32 hPa, respectively. To study the effect of reaction products, carbon dioxide with the values of initial partial pressure \( (P_{\text{CO}_2}^0) \) from 0 to 24.89 hPa was added to the reaction mixture. The distance between the catalyst surface and the illuminating lamps is 7 cm. The intensity of UV light varied in range 650–1147 lux. In order to change the light intensity the nets of different mesh sizes are placed between the light source and the catalyst film. Under these conditions the conversion of \( p \)-xylene (X) varied from 0.10 to 0.98.

The reaction rate on the studied catalysts was calculated by Temkin’s formula [29]

\[
r = \frac{C_{\text{xyl}}^0 \nu X}{m} (\text{mmol} \times \text{g}^{-1} \times \text{h}^{-1}), \tag{7}
\]
or

\[
r = \frac{P_{\text{xyl}}^0 \nu X}{24.436 m} (\text{mmol} \times \text{g}^{-1} \times \text{h}^{-1}), \tag{8}
\]
where $C_0$ and $P_0$ are the initial concentration ($\text{mmol} \times \text{l}^{-1}$) and initial partial pressure (hPa) of $p$-xylene in the gas mixture, respectively, $X$ is the $p$-xylene conversion, $m$ is the catalyst loading mass (g), and $v$ is the total flow velocity of reaction gas mixture ($1 \times \text{h}^{-1}$).

The convex shape of the curves reaction rate ($r$) versus conversion extent ($X$) on figure 13 shows that the reaction was inhibited by the substances participating in the reaction.

The dependence of the reaction rate on the partial pressures of substances involved in reactions is shown on figures 14 and 15. It can be seen from figures 14 and 15 that the graphs describing the dependence reaction rate ($r$)-partial pressure of $p$-xylene ($P_{\text{xyl}}$) and oxygen ($P_{\text{O}_2}$) are gently arched in first case and almost linear in second case, that means probably the terms $P_{\text{xyl}}$ and $P_{\text{O}_2}$ are present in both the numerator and the denominator of the equation, but the quantity of $k_1 P_{\text{O}_2}$ and $k_3 P_{\text{xyl}}$ in denominator is relatively small or can be present only in the numerator of the equation with the reaction order of 1.

The curves expressing the dependence of the reaction rate on concentration of water vapor (figure 16) have extreme shapes. At low concentrations of water vapor the reaction rate increases with the concentration of the given reactant, but reaches maximum values in the range of $P_{\text{H}_2\text{O}} = 11 - 20\text{hPa}$, after that gradually decreases when the concentration of the considered reactant continues to grow.

This allows us to drive a common rule for the reaction that the concentration/pressure of water vapor is involved in both numerator and denominator of the kinetic equation, but the value of its exponent in the denominator must be greater than that in the numerator.
Figure 5. UV–vis absorbance of P25-450-2 sample.

Figure 6. Plots of the transformed Kubelka-Munk function versus the energy of the light absorbed for P25-450-2 sample.

Figure 7. FTIR spectrum of P25-450-2 sample.
The coincidence of the curves showing the change of reaction rate with the degree of conversion (figure 17) at different CO₂ initial concentrations confirms that CO₂ does not affect the reaction rate. The dependence of the reaction rate on the light intensity is shown in figure 18.

From the presented above kinetic results the following conclusions should be drawn:

+ The reaction is inhibited by the substances of reaction (p-xylene/oxygen/water) and the kinetic equation is not exponential;
+ The quantities Pₓyl and P₀₂ can be present in both the numerator and the denominator of the equation, but quantity of k₁P₀₂ and k₃Pₓyl in denominator is relatively small or present only in the numerator with exponent 1;
+ Quantity P₇₆ is present both in the numerator and the dominator of the kinetic equation with its exponent in the numerator smaller than in the denominator;
+ Quantity P₇₇ does not participate in the kinetic equation.
+ Reaction rate is proportional to light intensity.

By-products formed during photocatalytic oxidation of p-xylene were analyzed directly from the reaction gas mixture (figure 19) and showed that the by-product is 4-metylbenzaldehyde presenting as traces. Thus, when considering the reaction kinetics the by-products could be ignored. In addition, the material equilibrium data for C also shows that only the product is CO₂.

For the rates of photo-oxidation of chloroform in aqueous suspension of TiO₂ the following kinetic equation has been proposed by Kormann et al [30]:

\[
- \frac{d[Red]}{dt} = - \frac{d[Ox]}{dt} = k_0 \theta_{Red} \theta_{Ox}.
\]  

(9)

In this equation quantity \( \theta_{Red} \) and \( \theta_{Ox} \) respectively are the fraction of adsorption of the electron-donating reductant and electron-accepting oxidant to the catalyst surface, and \( k_0 \) is reaction rate constant.

Because \( E_G \) of P25-450-2 catalyst is 3.155 eV, under the irradiation of UV light, its electron was excited from valence band to the conduction band (\( e_{CB}^- \)) generating a positive hole in the valence band (\( h_{VB}^+ \))

\[
TiO₂ + hv(\geq E_G) \rightarrow h_{CB}^+ + e_{CB}^-.
\]  

(10)
Next, hydroxyl radicals ($\cdot$OH), a strong oxidizing agent, are formed by oxidation of water molecules adsorbed on the surface of TiO$_2$ and –OH group (as seen in IR spectra) by photogenerated holes [31]:

$$h_{\text{VB}}^+ + \text{Ti}^{4+} - \text{OH} \rightarrow \text{Ti}^{4+} + \cdot\text{OH}.$$  \hspace{1cm} (11)

Electrons in the conduction band can be trapped by molecular oxygen adsorbed on the surface of TiO$_2$ P25 to form superoxide radical anion ($O_2^{-}$) [31]:

$$\text{Ti}^{4+} + e_{\text{CB}}^{-} \rightarrow \text{Ti}^{3+}.$$  \hspace{1cm} (13)
Figure 13. Variation of reaction rate ($r$) with conversion extent ($X$) of p-xylene at 40 °C on P25-450-2 thin film. Reaction conditions: $p_{O_2} = 105$ hPa; $p_{xyl} = 3.9$ hPa; $p_{H_2O} = 11$ hPa, and $p_{CO_2} = 0$ hPa.

Figure 14. Variation of reaction rate ($r$) with partial pressure of p-xylene ($p_{xyl}$) at 40 °C on P25-450-2 thin film. Reaction conditions: $p_{O_2} = 105$ hPa; $p_{H_2O} = 11$ hPa, $p_{CO_2} = 0$ hPa, and $X = 0.4$.

Figure 15. Variation of reaction rate ($r$) with partial pressure of oxygen ($p_{O_2}$) on P25-450-2 thin film. Reaction conditions: $T = 40$ °C; $p_{xyl} = 3.9$ hPa; $p_{H_2O} = 11$ hPa; $p_{CO_2} = 0$ hPa, and $X = 0.4$.

Figure 16. Variation of reaction rate ($r$) with partial pressure of water vapor ($p_{H_2O}$) on P25-450-2 thin film. Reaction conditions: $T = 40$ °C; $p_{xyl} = 3.9$ hPa; $p_{O_2} = 105$ hPa; $p_{CO_2} = 0$ hPa, and $X = 0.4$.

Figure 17. Variation of reaction rate ($r$) with conversion degree ($X$) at different values of carbon dioxide initial partial pressure ($p_{CO_2}^0$) on P25-450-2 thin film. Reaction conditions: $T = 40$ °C; $p_{xyl} = 3.9$ hPa; $p_{O_2} = 105$ hPa; and $p_{H_2O} = 11$ hPa.

Figure 18. Variation of reaction rate ($r$) with intensity of UV light irradiation ($I_a$) on P25-450-2 thin film. Reaction conditions: $T = 40$ °C; $p_{xyl} = 3.9$ hPa; $p_{O_2} = 105$ hPa; $p_{H_2O} = 11$ hPa; and $p_{CO_2} = 0$ hPa.
\[
\text{Ti}^{3+} + \text{O}_2 \rightarrow \text{Ti}^{4+} + \text{O}_2^{-}. \quad (14)
\]

Further, these powerful oxidants (hydroxyl radicals and reactive oxygen species) participate in the reaction with organic compounds to form \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) [32]:

\[
\cdot\text{OH} + \text{pollutant} \rightarrow \text{CO}_2 + \text{H}_2\text{O}, \quad (15)
\]

\[
\text{O}_2^{-} + \text{pollutant} \rightarrow \text{CO}_2 + \text{H}_2\text{O}. \quad (16)
\]

So, oxidant in the case of photo-oxidation in gas phase is both \( \cdot\text{OH} \) forming from dissociative adsorbed water and \( \text{O}_2^{-} \) generating from adsorbed molecular oxygen. Then, \( \theta_{\text{Ox}} \) in this case equal

\[
\theta_{\text{Ox}} = \theta_{\text{H}_2\text{O}}^{0.5} + \theta_{\text{O}_2}. \quad (17)
\]

When considering the near-linear dependence of the reaction rate on the partial pressure of \( p-\text{xylene} \), the question is whether the reaction proceeds according to the Langmuir-Hinshelwood or Eley-Rideal mechanisms? Turchi and Ollis [31] studied two reaction schemes in which the authors considered either the attack of an adsorbed hydroxyl radical on an adsorbed organic substrate [31] and the reactions (15) and (16) are the rate-determining steps, the rate of reaction (6) could be written in a following form

\[
r = k' \theta_{\text{Ox}} (\theta_{\text{O}_2} + \theta_{\text{H}_2\text{O}}^{0.5}), \quad (18)
\]

where \( k' \) is the rate constant, \( \theta_{\text{Ox}} \) and \( \theta_{\text{O}_2} \) are the fraction of the \( p-\text{xylene} \) and oxygen molecules adsorbed to the catalyst surface, respectively, \( \theta_{\text{H}_2\text{O}}^{0.5} \) is the fraction of the water dissociative adsorbed to the surface.

Mills et al [33] indicated that the constant of proportionality \( k_5 \) of the photo-mineralization of organic substrates \( S \) by oxygen on \( \text{TiO}_2 \) catalyst in following kinetic equation

\[
r = -\frac{d[S]}{dt} = \frac{k_5 K_S [S]}{1 + K_S [S]}, \quad (19)
\]

is proportional to the rate of light absorption \( I_a^\beta \) as well as the fraction of \( \text{O}_2 \) non-competitive adsorption at \( \text{Ti}^{4+} \) sites. In this equation \( r \) is the reaction rate, \( k_5 \) is the kinetic constant, \( K_S \) and \( [S] \) respectively are the adsorption equilibrium constant and concentration of substrate \( S \). The exponent \( \beta \) was 0.5 when the light intensity was high but equal to 1 at low light intensity values. Therefore, the kinetic equation (18) can be written as

\[
r = k\theta_{\text{O}_2} (\theta_{\text{O}_2} + \theta_{\text{H}_2\text{O}}^{0.5}) I_a^\beta \quad (20)
\]

where \( \theta_i \) is the degree of coverage of the respective species and \( I_a \) is total light intensity.
The fraction of adsorption of surfactants to the surface is determined by the following Langmuir formulae

\[
\theta_{\text{surf}} = \frac{K_{\text{surf}}P_{\text{surf}}}{1 + K_{\text{surf}}P_{\text{surf}} + K_{\text{O}_2}P_{\text{O}_2} + (K_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2} + K_{\text{CO}_2}P_{\text{CO}_2}},
\]

(21)

\[
\theta_{\text{O}_2} = \frac{K_{\text{O}_2}P_{\text{O}_2}}{1 + K_{\text{surf}}P_{\text{surf}} + K_{\text{O}_2}P_{\text{O}_2} + (K_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2} + K_{\text{CO}_2}P_{\text{CO}_2}},
\]

(22)

\[
\theta_{\text{H}_2\text{O}} = \frac{(K_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2}}{1 + K_{\text{surf}}P_{\text{surf}} + K_{\text{O}_2}P_{\text{O}_2} + (K_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2} + K_{\text{CO}_2}P_{\text{CO}_2}},
\]

(23)

where \( K_i \) is the Langmuir adsorption constant of the \( i \)-species on the surface of the catalyst and \( P_i \) is their partial pressure. Then, the final expression of the kinetics for the whole process of \( p \)-xylene photooxidation could be described as follows

\[
r = k' \frac{K_{\text{surf}}P_{\text{surf}}[aK_{\text{O}_2}P_{\text{O}_2} + (bK_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2}]}{[1 + cK_{\text{surf}}P_{\text{surf}} + dK_{\text{O}_2}P_{\text{O}_2} + (eK_{\text{H}_2\text{O}P_{\text{H}_2\text{O}}})^{1/2} + fK_{\text{CO}_2}P_{\text{CO}_2}]} \theta_{\text{surf}}^a
\]

(24)

where \( a, b, c, d, e, f \) are the constants.

Defining \( k'K_{\text{surf}} = k, aK_{\text{O}_2} = k_1, b^{1/2}K_{\text{H}_2\text{O}} = k_2, cK_{\text{surf}} = k_3, dK_{\text{O}_2} = k_4, e^{1/2}K_{\text{H}_2\text{O}} = k_5, fK_{\text{CO}_2} = k_6 \), and equation (24) can be written by follow common equation, in accordance with the above conclusions of the reaction kinetics:

\[
r = \frac{kP_{\text{surf}}^a[k_1P_{\text{O}_2}^b + k_2P_{\text{H}_2\text{O}}^c]^2}{(1 + k_1P_{\text{surf}}^{e_1} + k_2P_{\text{O}_2}^{e_2} + k_3P_{\text{H}_2\text{O}}^{e_3} + k_4P_{\text{surf}}^{e_4})^2}. \]

(25)

where \( r \) is reaction rate of \( p \)-xylene deep photooxidation; \( k, k_1, k_2, k_3, k_4, k_5, k_6 \) are constants of the kinetic equation; \( P_1 \) is partial pressure of the corresponding components; \( I_o \) is total light intensity; \( I_1, I_2, I_3, m_1, m_2, m_3, m_4 \) and \( \beta \) are reaction orders of the corresponding reagents and light intensity; and \( 2\alpha \) is surface coverage.

To determine the reaction order and the values of kinetic coefficients, the solver tool in MS excel was used to calculate the experimental data in combination with the following conditions: \( I_1 = I_2 = 0.2 \) (step 0.25), \( m_1 = m_2 = 0.2 \) (step 0.25), \( \alpha = 0 - 1 \) (step 0.25), \( m_3 \times 2\alpha > I_3 \).

The calculated results gave the best coincidence with the experimental data when: \( I_1 = I_2 = 1, I_3 = 0.5, m_1 = m_3 = m_4 = 1, m_2 = 0.5, \beta = 0.537 \) and \( \alpha = 1 \). The calculation also showed that \( k_1' = k_3 = 0 \). Therefore, the kinetic equation for the reaction can be written as follows

\[
r = \frac{kP_{\text{surf}}[k_1P_{\text{O}_2} + k_2P_{\text{H}_2\text{O}}^{0.5}]^{0.537}}{(1 + k_2'P_{\text{H}_2\text{O}}^{0.5} + k_4P_{\text{surf}})^{0.5}}. \]

(26)

The values of the kinetic constants in equation (26) are presented in table 2.

As it follows from table 2, the value of \( k_3 \) is very small in comparison with \( k_2' \) and equation (26) becomes

\[
r = \frac{kP_{\text{surf}}[k_1P_{\text{O}_2} + k_2P_{\text{H}_2\text{O}}^{0.5}]^{0.537}}{(1 + k_2'P_{\text{H}_2\text{O}}^{0.5} + k_4P_{\text{surf}})^{0.5}}. \]

(27)

The form of equation (26) showed that, the reaction takes place in the areas of high coverages. The exponent value \((1/\beta)\) of light intensity in kinetic equation (26) is found to be 0.537. According to the authors [17–19], the order of photon flux (\( \beta \)) for photocatalytic degradation of trichloroethylene in gas-phase over TiO\(_2\) supported on glass bead depends on the intensity and wavelength of light, varying from 0.42 to 1.0. The square-root dependence of reaction rate of chloroform photodegradation in the presence of O\(_2\) on light intensity was reported by Kormann et al [30]. This relationship was explained by the role of hydroxyl radical in the capture of holes and the initiator of oxidation of electron-donating substrates. In our investigation, as it follows from table 2, the value of coefficient \( k_3 \) of equation (26) is higher than \( k_1 \) about 28 times.

The extreme form of the dependence of the reaction rate on the partial pressure of water vapor, as shown in figure 16, is the result of the squared of the denominator of equation (26). When the concentration of water vapor \( P_{\text{H}_2\text{O}} \) is low, i.e. \( k_2'P_{\text{H}_2\text{O}}^{0.5} \) in the denominator of equation (26) is negligible compared to 1 and it follows that \( r \) is proportional to \( P_{\text{H}_2\text{O}} \) that means the reaction order of water vapor is +0.5. At high partial pressures of water vapor, the degree of surface coverage \( \theta_{\text{H}_2\text{O}} \) is high, i.e. \( k_2'P_{\text{H}_2\text{O}}^{0.5} \) in the denominator of equation (26) is much higher than 1 and the rate equation is proportional to \( 1/P_{\text{H}_2\text{O}} \), that means the reaction order of water vapor is −0.5. It was reported [13] that the concentration of water vapor in the gas mixture initially favored the photocatalytic process, but an increase in the water content reduced the rate of removal of acetone for a longer reaction time.

Therefore, the chosen kinetic model should be based on the Langmuir-Hinshelwood mechanism, in which the interaction between adsorbed \( p \)-xylene with molecular chemisorbed oxygen \( \text{O}_2 \) and radical \( \bullet\text{OH} \) is a rate-determining step.

All the points of view discussed above also lead to the conclusion that the nature of the catalytic action for photooxidation of \( p \)-xylene on TiO\(_2\) should be considered as a

| Table 2. Values of the kinetic constants in equation (26). |
|-------------------|-------|-----------|
| \( k \) \( \text{mmol} \times \text{g}^{-1} \times \text{h}^{-1} \times \text{lux}^{-0.537} \times \) | \text{Value} |
| \( k_1 \) \( \text{hPa}^{-1} \) | 1.917 \times 10^{-2} |
| \( k_2 \) \( \text{hPa}^{-0.5} \) | 0.639 \times 10^{-3} |
| \( k_3 \) \( \text{hPa}^{-1} \) | 1.677 \times 10^{-2} |
| \( k_4 \) \( \text{hPa}^{-1} \) | 4.00 \times 10^{-2} |
| Variance \( \% \) | 20.5 |
heterogeneous catalytic reaction involving \(O_2^\cdot\) and free radicals \(^*\)OH generated under the light irradiation.

4. Conclusion

It can be concluded that thermal treatment has a meaningful effect on TiO\(_2\) degussa P25 properties and performance. Calcination at 450 °C for 2h is able to create TiO\(_2\)-P25 of small nanoparticle size and low band gap energy, causing it to be a highly active and stable bare TiO\(_2\) catalyst for gas-phase photooxidation of \(p\)-xylene under ultraviolet light. The kinetic equation (26) based on Langmuir-Hinshelwood mechanism is the kinetic equation for gas-phase photooxidation reaction of \(p\)-xylene on TiO\(_2\)-P25 catalysts under UV light radiation. On TiO\(_2\)-P25, the photoreaction proceeds in the regions of high coverages; \(p\)-xylene and oxygen participate in the reaction in molecular adsorbed phase; water vapor is involved in the reaction in the forms of \(^*\)OH and \(H^+\). The reaction rate is proportional to concentration of \(p\)-xylene and oxygen. The effect of water vapor on the reaction rate is positive in the region of low concentrations and is negative in the high-concentrations region.

Acknowledgment

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2016.01.

References

[1] Awati P S, Awate S V, Shah P P and Ramaswamy V 2003 Catal. Commun. 4 393
[2] Bae H S and Im S 2004 Thin Solid Films 469–70 75
[3] Barakat M A, Schaeffer H, Hayes G and Ismat-Shah S 2005 Appl. Catal. B 57 23
[4] Bickley R I, Gonzalez-Carreno T, Lees J S, Palmisano L and Tilley R J D 1991 J. Solid State Chem. 92 178
[5] Ohno T, Sarukawa K, Tokieda K and Matsumura M 2001 J. Catal. 203 82
[6] Sopyan I 2007 Sci. Technol. Adv. Mater. 8 33
[7] Heynderickx P M, Thibaut J W, Poelman H, Poelman D and Marin G B 2009 Appl. Catal. B 90 295
[8] Kuipers E W, Vardi A, Danon A and Amirav A 1991 Phys. Rev. Lett. 66 116
[9] Stampfl C and Scheffler M 1997 Phys. Rev. Lett. 78 1500
[10] Tripa C E and Yates J T Jr 1999 Nature 398 591
[11] Baxter R and Hu P 2002 J. Chem. Phys. 116 4379
[12] Peral J, Domenech X and Ollis D F 1997 J. Chem. Technol. Biotechnol. 70 117
[13] Jaime J B, Domenech X and José P 1999 Revista Int. Contaminación Ambiental 15 7
[14] Idriss H, Miller A and Seebauer E G 1997 Catal. Today 33 215
[15] Preis S, Falconer J L, Asensio Rd P, Santiago N C, Kachina A and Kallas J 2006 Appl. Catal. B 64 79
[16] Kim S B, Cha W S and Hong S C 2002 J. Ind. Eng. Chem. 8 162
[17] Ollis D F, Pelizzetti E and Serpone N 1991 Environ. Sci. Technol. 25 1522
[18] Wang K H, Tsai H H and Hsieh Y H 1998 Appl. Catal. B 17 313
[19] Jacoby W A, Blake D M, Noble R D and Koval C A 1995 J. Catal. 157 87
[20] Luu C L, Nguyen Q T, Ho S T and Nguyen T 2013 Adv. Nat. Sci. 4 035003
[21] Sreeethawong T, Suzuki Y and Yoshikawa S 2005 J. Solid State Chem. 178 329
[22] Reyes-Coronado D, Rodriguez Gattorno G, Espinosa Pesqueira M, Cab C, de Coss R and Oskam G 2008 Nanotechnology 19 145605
[23] Su R, Bechstein R, So L, Vang R T, Sillassen M, Esbjornsson B, Palmqvist A and Besenbacher F 2011 J. Phys. Chem. C 115 24287
[24] Cullity B D 1978 Elements of X-Ray Diffraction (Reading, MA: Addison-Wesley)
[25] Sun B and Smirniotis P G 2003 Catal. Today 88 49
[26] Wang S, Zhao L, Wang W, Zhao Y, Zhang G, Ma X and Gong J 2013 Nanoscale 5 8882
[27] Duffy J A 1989 J. Am. Ceram. Soc. 72 2012
[28] Bergman A 1990 J. Am. Ceram. Soc. 73 2564
[29] Temkin M 1976 Kinetic and Catalysis 17 1095
[30] Kormann C, Bahmann D and Hoffmann M R 1991 Environ. Sci. Technol. 25 494
[31] Turchi C S and Ollis D F 1990 J. Catal. 122 178
[32] Pelaez M, Nolan N T, Pillai S C, Seery M K, Falaras P, Kontos A G, Dunlop P S, Hamilton J W, Byrne J A and O’shea K 2012 Appl. Catal. B 125 331
[33] Mills A and Le Hunte S 1997 J. Photochem. Photobiol. A 108 1