

Comparative studies of heterogeneous photocatalytic oxidation of heptane and toluene on pure titania, titania–silica mixed oxides and sulfated titania

Chao Xie, Zili Xu*, Qiuqing Yang, Na Li, Defeng Zhao, Debao Wang, Yaoguo Du

College of Environment and Resources, Jilin University, Changchun 130023, China

Received 11 January 2004; received in revised form 25 March 2004; accepted 25 March 2004

Abstract

Gas–solid heterogeneous photocatalytic oxidation (PCO) of heptane and toluene over UV-illuminated pure titania, titania–silica mixed oxides and sulfated titania was investigated at room temperature in a batch reactor. By comparing the photocatalytic activities of the different catalysts, we draw the following two conclusions: (1) there is no clear relationship between the crystalline phase and photocatalytic activity; (2) larger surface area is not always effective in the photocatalytic process and its effects on the photocatalytic activity strongly depend on the nature of the reactant used. In addition, the study on the behavior of catalyst deactivation and regeneration shows that titania–silica mixed oxide is deactivated more slowly than pure titania and sulfated titania, and for sulfated titania the regeneration temperature can be lowered due to the presence of SO_4^{2-} .

© 2004 Elsevier B.V. All rights reserved.

Keywords: Photocatalytic oxidation; Titania–silica mixed oxide; Sulfated titania; Heptane; Toluene; Deactivation; Regeneration

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 [1]. Moreover, the most significant problem related to the emission of VOCs is the possible production of photochemical oxidants. For example, the homogeneous photoreaction between alkane, such as heptane, and sulfur dioxide can induce photochemical smog [2]. Among the methods for the abatement of environment problems, heterogeneous photocatalytic oxidation (PCO) of air contaminants is one of the most attractive, due to the mild experimental conditions under which the runs are usually carried out. Hitherto, many researchers have reported that a variety of compounds can be decomposed with the aid of UV-illuminated semiconductors, such as TiO_2 , into CO_2 , H_2O and mineral compounds [3,4].

Toluene, as a major indoor and industrial air pollutant, has attracted considerable attention due to its noxiousness. For instance, previous literatures [5,6] investigated the PCO of toluene, which was mixed with air and water in various molar ratios, and found that the main oxidation product was benzaldehyde but benzene, benzyl alcohol, and traces of benzoic acid, phenol and unidentified compounds were also detected. Mendez–Roman and Cardona–Martinez have reported that benzaldehyde and benzoic acid were found on the surface of the deactivated photocatalysts by using in situ FT-IR spectroscopy and GC/MS. They concluded that benzaldehyde, as the main partial oxidation product, was further oxidized to benzoic acid, which was strongly adsorbed on the surface of the catalysts and responsible for the catalyst deactivation [7]. Furthermore, some researchers investigated the PCO of toluene and other organic compounds by using pure titania powder as the catalyst. Luo and Ollis [8] reported their initial study of both individual and simultaneous photocatalytic conversion of TCE and toluene. Einaga et al. [9] studied gas–solid heterogeneous photocatalytic decomposition of benzene, toluene and cyclohexane and cyclohexene over TiO_2 and their reactivities were compared.

* Corresponding author. Tel.: +86-4318503995; fax: +86-4318923907.
E-mail address: xuzl@mail.jlu.edu.cn (Z. Xu).

In addition, Alberici and Jardim [10] investigated the gas-phase photocatalytic destruction of 17 VOCs including alkanes, aromatics, alcohols, ketones and ethers and finally concluded that all major classes of oxidizable air contaminants may be candidates for photocatalytic destruction with TiO_2 .

The photocatalysts used in most of the above studies were pure titania without any modification. As we have known, TiO_2 has some disadvantages, such as its lower photoactivity. Therefore, recently many efforts have been devoted to improve the photocatalytic activity by various methods and the most widely used is to mix TiO_2 with some other oxides to form mixed oxides. Among these mixed oxides titania–silica mixed oxides have drawn considerable attention because mixing TiO_2 with SiO_2 is effective in enhancing the surface area, thermal stability and surface acidity and consequently the photocatalytic activity [11,12]. Recently, many studies regarding titania–silica mixed oxides have been reported [13–15]. However, there are also some limitations in the studies regarding titania–silica mixed oxides. Most of these studies only adopted one compound as the model reactant, and seldom compared the photocatalytic activity of titania–silica mixed oxides with that of other catalysts such as pure titania and sulfated titania. As we have known, it is important to study the photooxidation of various types of compounds with different catalysts in order to practically utilize the photocatalytic oxidation. Furthermore, as a major problem in the practical application, the behavior of deactivation and regeneration should be focused on. But, to the best of our knowledge, the study regarding deactivation and regeneration of titania–silica mixed oxide and sulfated titania is very limited. Therefore, to better understand the effects of the reactant used on the photocatalytic activity, we individually investigated PCO of two different compounds involving alkane (heptane) and aromatic compound (toluene) with the aid of UV-illuminated pure titania, titania–silica mixed oxides and sulfated titania in a batch reactor without water vapor. Moreover, the behavior of deactivation and regeneration of pure titania, titania–silica mixed oxide and sulfated titania during the PCO of toluene was investigated and compared.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Preparation of pure titania and titania–silica mixed oxides

All chemicals used in this study were used as received without any further purification. Titania–silica mixed oxides were prepared by using ammonia water (NH_3 , 28%) as the hydrolysis catalyst. Titanium tetrabutoxide (TBOT, $\geq 98\%$) and tetraethyl orthosilicate (TEOS, $\geq 98\%$) were selected as the source of titania and silica, respectively. Here, we give a typical procedure for the preparation of

titania–silica mixed oxide containing 16.6 mol% silica. First, 17.0 ml TBOT was mixed with 5.1 ml acetylacetone and 10.0 ml anhydrous alcohol. Secondly, 2.25 ml TEOS was mixed with the solution containing 10.8 ml bidistilled water, 23.9 ml ammonia water and 20.0 ml anhydrous alcohol under stirring. After a few minutes, the solution changed to opaque white due to the formation of dense Si sol. The final step was to simultaneously and slowly add Ti and Si sols into the beaker containing 10.0 ml anhydrous alcohol under stirring.

After all the above operations were finished, the samples were aged in the beaker covered by plastic film for 72 h. Finally, the samples obtained were evaporated and dried under infrared lamp, followed by calcination at the certain temperature for 2 h in air, and then ground into fine powders. Titania–silica mixed oxides with different silica concentration were obtained by only varying the dosage of TEOS. A pure titania sample was prepared by the same procedure illustrated above, except no TEOS was added into the Si sol.

2.1.2. Preparation of sulfated titania

First, white precipitate A was obtained by slowly adding NaOH solution into $\text{Ti}(\text{SO}_4)_2$ solution (the mol ratio of NaOH to $\text{Ti}(\text{SO}_4)_2$ is 1:8.402) under vigorous stirring. After centrifuged and washed many times until the supernatant liquid was neutral, the precipitate A was dissolved in HNO_3 solution to form colloid, and then heated in a water-bath to form precipitate B. The precipitate B was aged for 24 h and then centrifuged and washed many times until the supernatant liquid was neutral. Finally the precipitate B was dried as for the pure titania and titania–silica mixed oxides and calcined at 300 °C for 2 h.

In this paper, pure titania, titania–silica mixed oxides and sulfated titania were labeled as TiO_2-T , $\text{TiO}_2-X\text{SiO}_2-T$ and $\text{SO}_4^{2-}/\text{TiO}_2-T$, where X denotes mol% of silica in the titania–silica mixed oxides and T the calcination temperature.

2.2. Catalysts characterization

Surface area values of the prepared samples were determined by nitrogen physisorption data at 77 K using a Micromeritics ASAP 2010 and calculated by BET method. The crystalline phases of the samples were characterized by a Bruker D8 GADDS X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The phase content of the catalyst can be calculated from the integrated intensities of anatase (1 0 1) and rutile (1 1 0) peaks. The mass fraction of rutile (W_R) can be calculated from [16]

$$W_R = \frac{A_R}{0.886A_A + A_R}$$

where A_A and A_R represent the integrated intensities of the anatase (1 0 1) and rutile (1 1 0), respectively.

2.3. Photocatalytic activity tests

The photocatalytic activity experiments were carried out at room temperature using a 300 ml quartz reactor. In the experiment, 0.1 g catalyst was spread uniformly over the internal surface of the reactor. After this, the reactor was vacuum-packed and then suitable amount of reactant (0.1 or 0.4%), oxygen (20%) were injected into the reactor. Finally ultrapurity nitrogen was mixed with the reactant in the reactor to 1 atm pressure. After adsorption equilibrium was reached, as measured by GC, the reaction was started by turning on a 400 W high-pressure mercury lamp. The primary wavelength distribution of this lamp is at 365 nm and the light intensity is 5.3 mW cm^{-2} at 15 cm away from the lamp. The concentration of reactant in the reactor was measured with a Hewlett–Packard 4890D gas chromatograph equipped with a flame ionization detector (FID) and the photocatalytic activity experiment of each run was lasted for 2 h. The yield of CO_2 was determined by GC equipped with a thermal conductivity detector (TCD) and a Porapak QS stainless-steel column. In the deactivation experiment, the catalysts were used on 10 consecutive runs (i.e., 20 h). Between each run the quartz reactor was vacuumed and then toluene (0.1%), oxygen (20%) and ultrapurity nitrogen were injected into the reactor.

In this paper, the conversion rate was calculated by $(C_0 - C)/C_0$, where C is the concentration of the reactant after irradiation as a function of reaction time, C_0 the concentration of the reactant after adsorption equilibrium and before the irradiation in the presence of catalyst. The adsorption rate towards the reactant was obtained by $(C_1 - C_0)/C_1$, where C_1 is the concentration of the reactant without catalyst and illumination, C_0 the same as that mentioned above.

3. Results and discussion

3.1. Characterization of the catalysts

The surface area values of the prepared photocatalysts are given in Table 1. It is clear that the presence of Si and SO_4^{2-} can stabilize the surface area values as calcined at higher temperature. Even after calcination at 800°C the surface

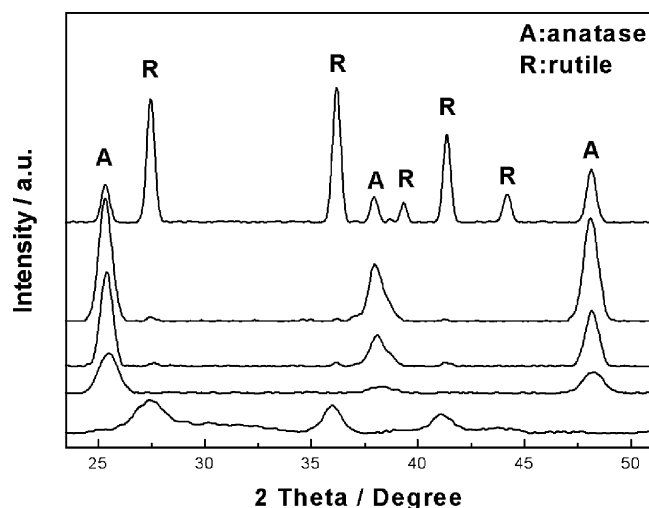


Fig. 1. The XRD patterns of the catalysts. From the top to the bottom of the graph: TiO_2 -600; TiO_2 -400; TiO_2 -9.1% SiO_2 -800; TiO_2 -9.1% SiO_2 -600; $\text{SO}_4^{2-}/\text{TiO}_2$ -300.

area of TiO_2 -9.1% SiO_2 presents a rather higher value of 80.4. Moreover, the surface area of TiO_2 -9.1% SiO_2 -600 is higher than that of TiO_2 -7.7% SiO_2 -600, which is in agreement with the previous reports that the surface area of titania-silica mixed oxide is monotonically increased with the increase of Si concentration [17,18].

Fig. 1 shows the XRD patterns of the catalysts calcined at different temperatures. Upon calcination at 400°C for 2 h, pure titania exhibits stronger anatase diffraction peaks of (1 0 1), (0 0 4) and (2 0 0) at 25.2° , 37.8° and 48.0° as well as the small rutile diffraction peaks of (1 1 0), (1 0 1) and (1 1 1) at 27.4° , 36.1° and 41.2° , indicating that TiO_2 -400 is the mixture of anatase (major phase) and rutile phase. As the calcination temperature is increased up to 600°C , the content of rutile is significantly increased. It can also be seen that TiO_2 -9.1% SiO_2 just begins to form rutile phase at about 800°C , which confirms that the suppression of phase transformation of titania from anatase to rutile resulting from the enhanced thermal stability. It is interesting to note that $\text{SO}_4^{2-}/\text{TiO}_2$ -300 is a pure rutile phase, while calcined at a relative low temperature. The crystalline phase contents of the catalysts are summarized in Table 1.

Table 1

The crystalline phase contents of the photocatalysts and conversion rates towards heptane and toluene oxidation^a

Samples	Surface area (m^2/g)	Phase content (%)	Heptane		Toluene	
			Ads. rate (%)	Conv. rate (%)	Ads. rate (%)	Conv. rate (%)
TiO_2 -400	116.7	A: 98.1, R: 1.9	18.1	99.6	57.5	22.5
TiO_2 -500	90.5	A: 83.7, R: 16.3	9.6	67.3	47.1	88.3
TiO_2 -9.1% SiO_2 -600	218.4	A: 100	34.3	99.8	66.6	92.5
TiO_2 -9.1% SiO_2 -800	80.4	A: 97.6, R: 2.4	7.9	57.7	44.5	97.4
TiO_2 -7.7% SiO_2 -600	190.6	A: 100	28.1	97.1	62.6	98.1
$\text{SO}_4^{2-}/\text{TiO}_2$ -300	219.0	R: 100	59.7	99.2	85.0	96.0

^a A and R denote anatase and rutile, respectively. Ads. rate and Conv. rate represent adsorption rate and conversion rate, respectively. Here, the conversion rates were obtained after the catalysts were irradiated for 1 h.

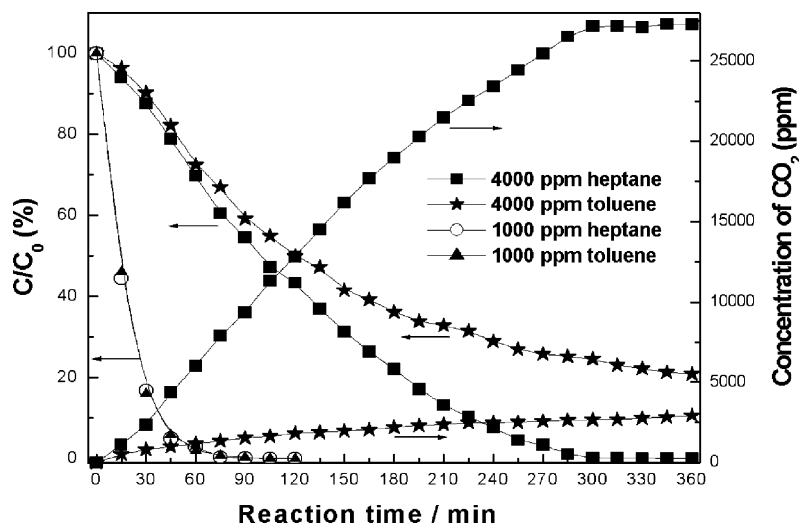


Fig. 2. The comparisons of PCO of 1000 and 4000 ppm heptane and toluene, and the CO₂ evolution during the PCO of 4000 ppm heptane and toluene.

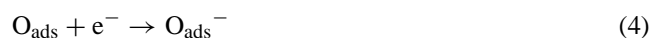
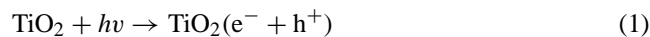
3.2. Comparison of the photoactivities of heptane and toluene on different catalysts

To fully understand the difference occurred in the course of PCO of heptane and toluene, we show the time courses for the PCO of heptane and toluene (concentration 1000 and 4000 ppm) by using TiO₂-7.7% SiO₂-600 as catalyst in Fig. 2. We can see that the photocatalytic activity of 1000 ppm heptane is essentially equal to that of 1000 ppm toluene during the overall 120 min photoreaction. However, the photocatalytic activities of 4000 ppm heptane and toluene are apparently lower than those of 1000 ppm heptane and toluene. This phenomenon illustrates that much higher concentration of reactant can lower the photoactivity in that too much active sites are covered by the intermediates produced during the photoreaction. It should be noted that the photocatalytic activity of 4000 ppm toluene is obviously lower than that of 4000 ppm heptane after irradiation of 60 min, while before irradiation of 60 min their photoactivities are essentially similar. After irradiation of 300 min 4000 ppm heptane is photooxidized completely and about 97.4% heptane is photodegraded into CO₂ (about 27,000 ppm). As for toluene, after irradiation of 360 min 4000 ppm toluene is not completely photooxidized and the yield of CO₂ is only about 2900 ppm which is about 10-fold smaller than that of 4000 ppm heptane, meaning that only about 10.3% 4000 ppm toluene is completely photodegraded into the final product CO₂. Additionally, the catalyst does not change the color at the end of photooxidation of heptane, however, in the case of toluene the catalyst turns from white to yellow. Based on the results illustrated above, we can infer that the catalyst surface is clean after photoreaction with heptane since heptane could be photooxidized completely and rapidly into the final product CO₂. In contrast, toluene is much difficult to be completely and rapidly photooxidized into CO₂ and the catalyst surface is occupied by the less-reactive intermediates which can lower the

photocatalytic activity by blocking the active sites on the surface. In addition, all the later photoreaction experiments use 1000 ppm compound as the model reactant.

Table 1 summarizes the conversion rates of heptane and toluene on different catalysts. It is worthwhile to note that, in the case of titania-silica mixed oxides, the effects of Si concentration on the photocatalytic activity are notably different when two different compounds are used as the model reactant. We can see that the photocatalytic activity of TiO₂-9.1% SiO₂-600 is higher than that of TiO₂-7.7% SiO₂-600 in the case of PCO of heptane, on the contrary TiO₂-7.7% SiO₂-600 shows higher photocatalytic activity than TiO₂-9.1% SiO₂-600 when toluene is used as the model reactant. It can be seen from Table 1 that the surface area of TiO₂-9.1% SiO₂-600 is larger than that of TiO₂-7.7% SiO₂-600. So we suppose that the difference in the photocatalytic activity between TiO₂-7.7% SiO₂-600 and TiO₂-9.1% SiO₂-600 as the two different reactants are used, could be explained by taking into account the variation of surface area and the different nature of two reactants used.

In order to better illustrate the effects of variation of surface area on the photocatalytic activity as different reactants are used, it is necessary for us to understand the basic mechanism of photocatalysis which is summarized in the following scheme (subscript ads represent adsorption):



When the photocatalyst absorbs photons having energy greater than its bandgap, electrons (e^-) are excited from the valence to the conduction band leaving holes (h^+) behind. In the absence of the electron and hole scavengers, most of them recombine with each other within a few nanoseconds. If the scavengers are present to trap the electrons and holes, the recombination of electron–hole pairs can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced [19]. In this case, oxygen adsorbed on the surface of the photocatalyst plays a significant role in the reaction with electrons, with O_2^- , O and O^- being the products of this electron transfer (reactions (2)–(4)) [20]. At the same time, photogenerated holes are trapped by surface hydroxyl groups, producing hydroxyl radicals (reactions (5) and (6)), which play important roles in photocatalytic reactions [19]. Moreover, reactions among O_2^- , O and H_2O_{ads} give rise to the formation of OH^\bullet and HO_{2ads}^\bullet , and HO_{2ads}^\bullet is another source of OH^\bullet [5,21]. In addition, it has been recognized that adsorption of reactants on the catalyst surface is a very important prerequisite for highly efficient detoxification in that reactants can themselves act as adsorbed traps for the photogenerated holes. From the above illustration we can see that PCO occurs via interfacial charge transfer between the photogenerated electrons and holes and the surface-adsorbed species. Larger surface area is beneficial not only for adsorbing more oxygen and surface hydroxyl groups to produce a higher content of active species (O_2^- , O, O^- and OH^\bullet), but also for adsorbing more reactants, which is in well agreement with the results listed in Table 1 that the catalyst with larger surface area shows higher adsorption ability towards the reactants, on the catalyst surface to trap the photogenerated holes. Therefore, it can be said that the greater is the surface area, the higher is the content of active species on the catalyst surface and the stronger is the adsorption ability towards the reactants, the higher is the photocatalytic activity. However, this conclusion may be true for the photooxidation of the compound, such as heptane. As shown previously, heptane can be completely and rapidly photooxidized into the final product CO_2 on the catalyst surface. Hence, larger surface area means more reactants can be adsorbed on the catalyst surface to hinder the recombination of electrons and holes through participating in the photoreaction and therefore the photocatalytic activity will be enhanced. On the contrary, for toluene which is rather difficult to be completely and rapidly photooxidized into CO_2 and can produce less-reactive poisonous intermediates, larger surface area means more surface active sites are occupied by the less-reactive poisonous intermediates, which is not beneficial for enhancing the photocatalytic activity.

Besides the concentration of Si in titania–silica mixed oxides, the calcination temperature also has obviously different effects on the photocatalytic activity when two different compounds are used as the model reactant. It can be seen from Table 1 that, when using heptane as model reactant, TiO_2-400 (A: 98.1%, R: 1.9%) shows higher

photoactivity as compared to TiO_2-500 (A: 83.7%, R: 16.3%). In contrast, in the case of toluene TiO_2-500 shows higher photocatalytic activity than TiO_2-400 . Similar phenomenon also occurs in the titania–silica mixed oxides. For PCO of toluene, $TiO_2-9.1\% SiO_2-800$ (A: 97.6%, R: 2.4%) exhibits higher photocatalytic activity with respect to $TiO_2-9.1\% SiO_2-600$ (A: 100%), while the photocatalytic activity of $TiO_2-9.1\% SiO_2-800$ for heptane is notably lower than that of $TiO_2-9.1\% SiO_2-600$. Moreover, note that SO_4^{2-}/TiO_2-300 with complete rutile phase shows much higher photoactivity towards both heptane and toluene. According to the above facts, we suggest that there is no clear correlation of crystalline phase with the photoactivity, and the effects of crystalline phase on the photocatalytic activity will depend on the nature of the reactant used. This conclusion lets us recall some disagreement regarding the relationship between the crystalline phase and photocatalytic activity. For instance, some studies confirmed that the anatase phase of titania is more active than rutile [22,23]. However, other studies claimed that a mixture of anatase and rutile is more active than pure anatase [24–26]. As we have known, titania has three different crystalline phase: anatase, rutile and brookite, rutile among which is the thermodynamically stable state, while the other two phases are metastable. Generally, anatase phase titania obtained by calcined at lower temperature should have larger surface area, and with the transformation from anatase to rutile phase the surface area of the catalyst will be evidently reduced due to the calcination at higher temperature. Based on the different performance of heptane and toluene in the course of PCO process, we deduce that pure anatase phase with large surface area will be better for PCO of heptane, while as for toluene a mixture of anatase and rutile with smaller surface area may be better for obtaining higher photocatalytic activity. In addition, in comparison with heptane, PCO of toluene needs the catalyst calcined at higher temperature to obtain good photocatalytic activity. In order to reduce the amount of less-reactive intermediates adsorbed on the catalyst surface, it is necessary to calcine the catalyst at higher temperature to reduce the catalyst surface area. Therefore, it can be concluded that larger surface area is not always effective in the PCO process and its effects on the photocatalytic activity strongly depend on the nature of reactant used as well.

It is worthwhile to note that titania–silica mixed oxide possesses relatively higher conversion rates towards heptane and toluene at rather high temperature (600–800 °C), illustrating that titania–silica mixed oxides can tolerate higher temperature, which can be explained as the consequence of enhanced thermal stability due to the addition of silica. Thus, titania–silica mixed oxides can be applied in a higher temperature environment at which pure titania significantly loses its photocatalytic activity. Furthermore, the enhanced thermal stability enables us to calcine the titania–silica mixed oxides at high temperature to reduce the bulk defects without the significant decrease of surface

area, which are helpful for improving the photocatalytic activity.

3.3. Deactivation and regeneration of the catalysts

Although semiconductor photocatalysts, such as TiO_2 , were proven to have wide application in PCO of different compounds, deactivation has been already reported to be a crucial disadvantage of this technique in practice [7,27,28]. However, none of studies regarding PCO of toluene operated in a batch reactor by using different catalysts reported catalyst deactivation. This result is plausible, as the changing concentration characteristic of batch operation could mask any relatively slower catalyst deactivation. As pointed out by Sauer and Ollis [29], deactivation would only be evident if repeat runs were made without catalyst pretreatment or regeneration between runs. To the best of our knowledge, such repeat run data are not reported in the gas–solid PCO system.

Fig. 3 shows the variations of conversion rates of TiO_2 -7.7% SiO_2 -600, TiO_2 -500 and $\text{SO}_4^{2-}/\text{TiO}_2$ -300 for the PCO of toluene with consecutive 10 runs (i.e., 20 h). We can see that the conversion rates decrease gradually and the order of photocatalytic activity is TiO_2 -7.7% SiO_2 -600 > TiO_2 -500 > $\text{SO}_4^{2-}/\text{TiO}_2$ -300 after the catalysts reach the steady-state characterized by a relative low conversion value.

It has been reported that the catalytic activity of TiO_2 could be maintained indefinitely under an abundance of water vapor since it can be adsorbed on the catalyst surface to form surface hydroxyl groups [10,20,30,31]. The surface hydroxyl groups exhibit their important influence on the photoreaction process not only through their direct participation in the photoreaction process (by trapping the charge transfer

reaching the catalyst surface to produce very reactive surface hydroxyl radicals) but also by affecting the adsorption of reactant molecules: on one hand, hydroxyl has been reported to be the active sites for toluene adsorption [32,33]; on the other hand, they may cover the sites (exposed titanium cations with unsaturated coordination) where electron trapping by adsorbed oxygen occurs. This process is important for producing the oxygen radicals active in toluene oxidation but also for hindering the recombination of electron–hole pairs that may limit the number of charge carriers available for the photocatalytic reaction [32]. Infrared spectroscopy studies during TCE oxidation show that the titania surface becomes partially dehydroxylated as the reaction proceeds [34]. So it is reasonable that the surface must be continuously dehydroxylated until the catalyst loses its activity completely if long-term photoreaction is to be maintained. However, the complete deactivation was not observed in our all photoreactions, indicating that surface hydroxyl groups should be regenerated. As we have known, toluene is rather difficult to be completely photodecomposed and can produce less-reactive poisonous intermediates. Moreover, in this study all photoreactions were operated in the absence of water vapor. Therefore, the catalyst deactivation could be attributed to the two following reasons: (1) the surface active sites were occupied by the less-reactive poisonous intermediates, which is supported by the fact that the catalysts turned from white to yellow, and with the increase of run number became more and more yellow until the catalysts reached the steady-state when TiO_2 -7.7% SiO_2 -600 and TiO_2 -500 were used as the catalysts; (2) surface hydroxyl groups were consumed.

The slowest deactivation of TiO_2 -7.7% SiO_2 -600 and its highest photocatalytic activity at steady-state can be attributed not only to its higher content of surface hydroxyl groups on the catalyst surface [14,35], but also to its

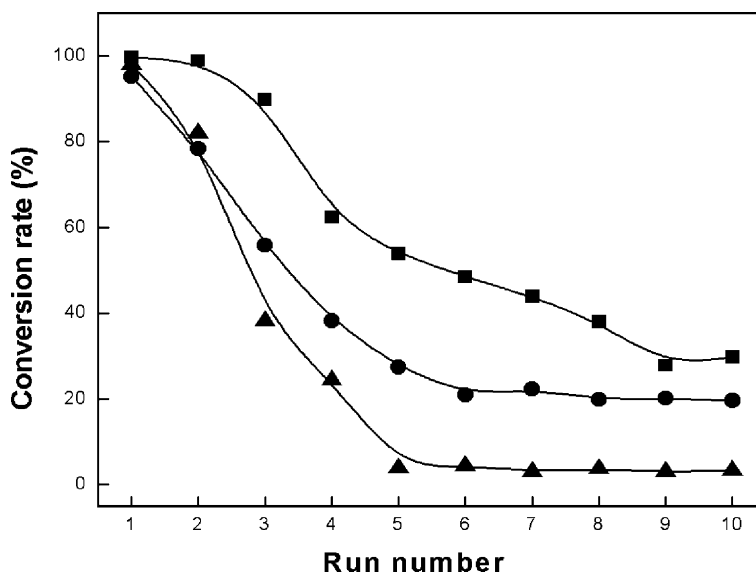


Fig. 3. The variations of conversion rates for different catalysts with run number by using toluene as the model reactant. TiO_2 -7.7% SiO_2 -600 (■); TiO_2 -500 (●); $\text{SO}_4^{2-}/\text{TiO}_2$ -300 (▲). Here, the conversion rates of each run number were obtained by irradiating the catalysts for 2 h.

stronger rehydroxylation ability. Although hydroxyl radicals sustain continuous consumption during photocatalysis, water formed as a product of the reaction may be the only source which can replenish the consumed hydroxyl radicals by adsorbed on the catalyst surface to rehydrate the catalyst. Hence, after used same run number TiO_2 -7.7% SiO_2 -600 should have higher content of surface hydroxyl radicals since the larger surface area of TiO_2 -7.7% SiO_2 -600 can adsorb more water molecules. Furthermore, a process for hydroxyl regeneration is the dissociation of water which requires the presence of pairs: one with acid character (low coordination titanium cations) to bind initially the water molecule and the other one with basic characteristics (exposed bridging oxygens) to accept the proton [36]. This cooperative effect of acid and basic sites can be obtained if the surface possesses an appropriate structural arrangement at the atomic scale. That is to say, modification of TiO_2 by SiO_2 may be an effective method to enhance the water dissociation ability of catalyst since it has been confirmed by many researchers that titania-silica mixed oxides can be significantly different from pure titania in physicochemical characteristics.

$\text{SO}_4^{2-}/\text{TiO}_2$ -300 is the most rapidly deactivated and after five runs its photocatalytic activity decreases down to a negligible value. This can be attributed to its higher adsorption ability due to its higher surface area, which confirms and reinforces the previous conclusion that larger surface area is not always effective in the photocatalytic reaction. On the other hand, note that the surface area values of TiO_2 -7.7% SiO_2 -600 and $\text{SO}_4^{2-}/\text{TiO}_2$ -300 are comparable, however, TiO_2 -7.7% SiO_2 -600 obviously deactivates slower than $\text{SO}_4^{2-}/\text{TiO}_2$ -300, implying that the presence of SO_4^{2-} may be detrimental to the rehydroxylation ability of the catalyst.

Table 2 lists the toluene conversion rates of fresh, deactivated and regenerated TiO_2 -500, TiO_2 -7.7% SiO_2 -600 and $\text{SO}_4^{2-}/\text{TiO}_2$ -300. In our study, in order to regenerate deactivated catalysts. TiO_2 -7.7% SiO_2 -600, TiO_2 -500 and $\text{SO}_4^{2-}/\text{TiO}_2$ -300 were calcined at 500, 400 and 300 °C in air for 1 h. After this heat treatment, it was found that the photocatalytic activity of TiO_2 -7.7% SiO_2 -600 is completely restored, while the photoreactivity of TiO_2 -500 is slightly lower than the initial, implying that there are still

some intermediates adsorbed on the catalyst surface after calcination at 400 °C. This confirms that the less-reactive poisonous intermediates adsorbed on the catalyst surface are responsible for the deactivation of catalysts, and the temperature required to completely recover the photoactivity should be between 400 and 500 °C, which is agreement with the report by Suib and co-workers that 420 °C was required to completely recover the catalytic activity of TiO_2 deactivated during the course of PCO of toluene [28]. So, it is interesting to note $\text{SO}_4^{2-}/\text{TiO}_2$ -300 is entirely restored at 300 °C. This illustrates that the presence of SO_4^{2-} facilitates the removal of less-reactive poisonous intermediates from the deactivated TiO_2 surface. The function of SO_4^{2-} may be identical to that of platinum loaded on TiO_2 catalyst which is known to be an excellent catalyst to complete oxidation of carbon species at low temperature [28]. In addition, note that loading platinum on TiO_2 lowers the regeneration temperature at the expense of some photoactivity. Therefore, we suggest that modification of TiO_2 by SO_4^{2-} is a promising technique, which can simultaneously lower the regeneration temperature and enhance the photocatalytic activity.

Fig. 4(a) and (b) shows the variations of adsorption rates and the yields of benzene as a function of run number, respectively. We can see that, although the catalysts undergo a decrease of adsorption rate with the increase of run number, finally they do not lose the adsorption ability totally. This confirms the previous conclusion that the surface hydroxyl groups must be regenerated because toluene molecules are adsorbed on the catalyst surface via the surface hydroxyl groups, and at the same time demonstrates that there should exist a balance between the depletion and regeneration of surface hydroxyl groups after the catalysts reach the steady-state.

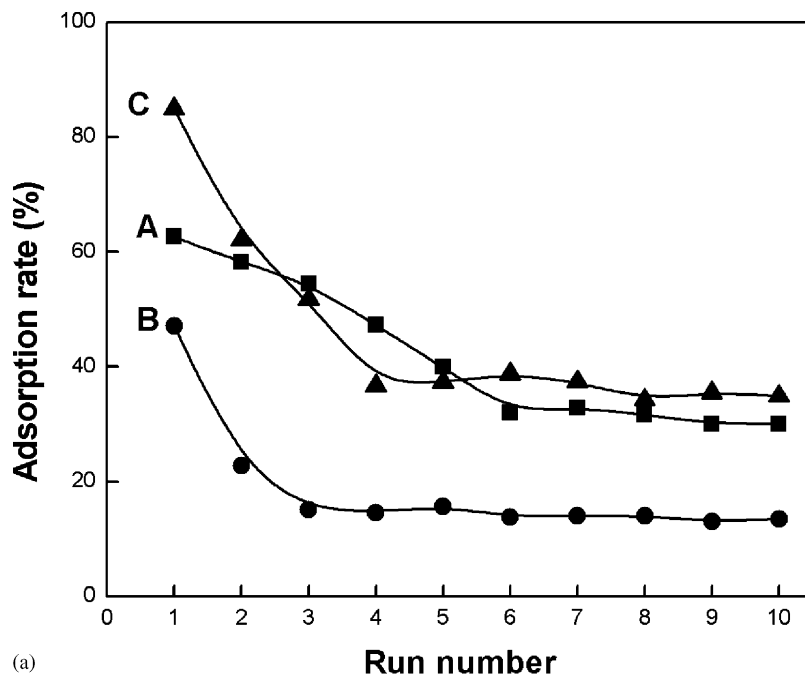
For three different catalysts, the yields of benzene increase with the run number and reach the maximum, and then decay with the further increase of run number, as shown in Fig. 4(b). It is worth to note that the yields of benzene reach the maximum right after catalysts initially reach their lowest adsorption rates. As we have known, benzene is derived from the further oxidation of benzaldehyde to benzoic acid and the subsequent photodecarboxylation [5]. The yield of benzene should be dependent on the concentration of benzoic acid on the catalyst surface. At the run number before the catalysts reach their lowest adsorption rates, the content of surface hydroxyl radicals should be higher enough to further oxidation of benzaldehyde to benzoic acid. Hence, the concentration of benzoic acid will be increased with the increase of run number and reach its maximum when the catalysts initially reach their lowest adsorption rates. Therefore, the yields of benzene increase with the increase of the concentration of benzoic acid on the catalyst surface. After the catalysts reach their lowest adsorption rates, the further oxidation of benzaldehyde to benzoic acid will not be proceeded because the surface hydroxyl radicals are largely consumed. The concentration of benzoic acid will drop down with the further increase of run number. So it is reasonable that the

Table 2

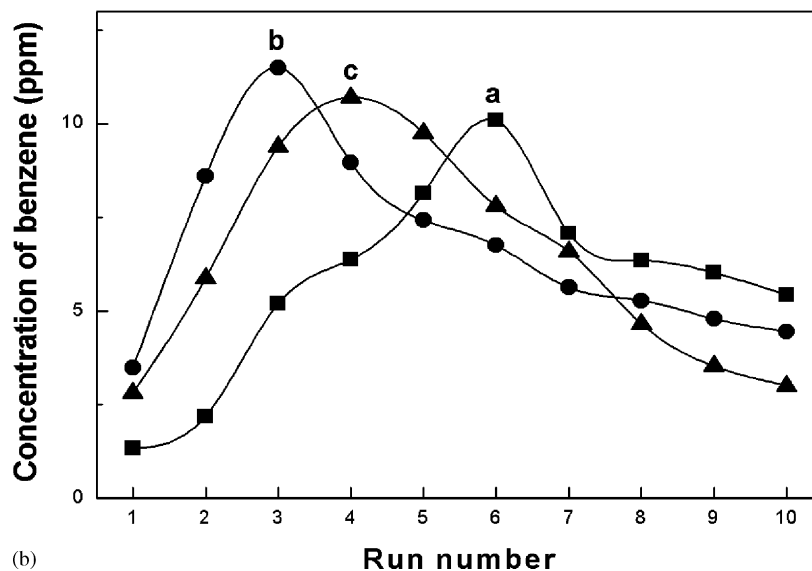
The toluene conversion rates of fresh, deactivated and regenerated pure titania, titania-silica mixed oxide and sulfated titania

Samples	Conversion rate ^a (%)		
	Fresh	Deactivated	Regenerated
TiO_2 -500	95.1	19.6	89.4
TiO_2 -7.7% SiO_2 -600	99.7	29.7	98.9
$\text{SO}_4^{2-}/\text{TiO}_2$ -300	97.8	3.1	97.5

^a The conversion rates of fresh and regenerated catalysts were obtained by irradiating the catalysts for 2 h. The conversion rates of the deactivated catalysts were obtained by using the catalysts after consecutive 10 runs (i.e., 20 h).



(a)



(b)

Fig. 4. The variations of toluene adsorption rates (depicted in (a)) and yields of benzene (depicted in (b)) as a function of run number. TiO₂-7.7% SiO₂-600 (A, a), TiO₂-500 (B, b), SO₄²⁻/TiO₂-300 (C, c).

yields of benzene will decay with the further increase of run number.

4. Conclusions

Gas–solid heterogeneous photooxidation of two compounds involving alkane (heptane) and aromatic compound (toluene) was investigated by the aid of UV-illuminated pure titania, titania–silica mixed oxides and sulfated titania in a batch reactor. When using different compounds as the model reactant, the effects of calcination temperature and

Si concentration in titania–silica mixed oxides on the photocatalytic activity are significantly different and strongly depend on the nature of the reactant used. In contrast with PCO of heptane, higher calcination temperature and smaller Si concentration in titania–silica mixed oxide should be better for obtaining higher photocatalytic activity in the case of PCO of toluene. This difference occurred in the course of PCO of heptane and toluene can be explained by the different nature of the two different reactants used. For heptane, which can be completely and rapidly photooxidized into the final product CO₂, catalyst with larger surface area obtained via calcining at relatively lower temperature

or adding a larger amount of Si into titania–silica mixed oxide should be beneficial for obtaining higher photoactivity. However, in the case of toluene, which is difficult to be photooxidized rapidly and completely into CO₂ and can produce less-reactive poisonous intermediates, catalyst with smaller surface area obtained through calcining at higher temperature or adding a smaller amount of Si into titania–silica mixed oxide should be better to improve the photocatalytic activity because smaller surface area can reduce the catalyst adsorption ability towards the less-reactive poisonous intermediates, which can be adsorbed on the catalyst surface active sites to reduce the photocatalytic activity. Therefore, we conclude that larger surface area is not always effective in the photocatalytic process and its effects on the photocatalytic activity strongly depend on the nature of the reactant used. In addition, we also found that there is no clear relationship between the crystalline phase and photocatalytic activity. That whether anatase or a mixture of anatase and rutile has better photoactivity is also dependent on the nature of the reactant used.

In the deactivation and regeneration experiments, the complete deactivation is not observed, indicating that the surface hydroxyl groups must be regenerated and there should exist a balance between the depletion and regeneration of surface hydroxyl groups after the catalysts reach the steady-state. Moreover, titania–silica mixed oxide is more active and appears to deactivate slower than pure titania and sulfated titania. This can be attributed to both its higher content of surface hydroxyl groups and stronger rehydroxylation ability. Meanwhile, the yields of benzene initially increase with the increase of run number and reach the maximum right after the catalysts reach their lowest adsorption rates, and then decrease with the further increase of run number. This may be related to the variation of benzoic acid concentration on the catalyst surface with the decrease of the content of surface hydroxyl radicals. In addition, modification of TiO₂ by SO₄²⁻ may be a promising technique, which can simultaneously lower the regeneration temperature and enhance the photocatalytic activity. Its disadvantage is the most rapid deactivation, which can be attributed to the stronger adsorption ability associated with its larger surface area and the presence of SO₄²⁻ which may be detrimental to the rehydroxylation ability of the catalyst.

Acknowledgements

This work was supported by a grant from the National Natural Science Foundation of China (no. 20277015).

References

- [1] P. Avila, A. Bahamonde, J. Blanco, B. Sanchez, A.I. Cardona, M. Romero, *Appl. Catal. B* 17 (1998) 75.
- [2] V.I. Makarov, G.I. Skubnevskaya, N.M. Bazhin, *Int. J. Chem. Kinet.* 13 (1981) 231.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [4] A.L. Linsebigler, G.Q. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735.
- [5] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B* 20 (1999) 15.
- [6] A. Navio, M. Garcia Gomez, M.A. Pradera Adrian, J. Fuentes Mota, *J. Mol. Catal.* 104 (1996) 329.
- [7] R. Mendez-Roman, N. Cardona-Martinez, *Catal. Today* 40 (1998) 353.
- [8] Y. Luo, D.F. Ollis, *J. Catal.* 163 (1996) 1.
- [9] H. Einaga, S. Futamura, T. Ibusuki, *Appl. Catal. B* 38 (2002) 215.
- [10] R.M. Alberici, W.F. Jardim, *Appl. Catal. B* 14 (1997) 55.
- [11] X.T. Gao, I.E. Wachs, *Catal. Today* 51 (1999) 233.
- [12] J.B. Miller, E.I. Ko, *Catal. Today* 35 (1997) 269.
- [13] X.Z. Fu, L.A. Clark, Q. Yang, M.A. Anderson, *Environ. Sci. Technol.* 30 (1996) 647.
- [14] K.Y. Jung, S.B. Park, *Appl. Catal. B* 25 (2000) 249.
- [15] C. Anderson, A.J. Bard, *J. Phys. Chem. B* 101 (1997) 2611.
- [16] J.G. Yu, J.C. Yu, M.K.-P. Leung, W.K. Ho, B. Cheng, X.J. Zhao, J.C. Zhao, *J. Catal.* 217 (2003) 69.
- [17] M. Galan-Fereres, L.J. Alemany, R. Mariscal, M.A. Banares, J.A. Anderson, J.L.G. Fierro, *Chem. Mater.* 7 (1995) 1342.
- [18] X.T. Gao, S.R. Bare, J.L.G. Fierro, M.A. Banares, I.E. Wachs, *J. Phys. Chem. B* 102 (1998) 5653.
- [19] D.R. Park, J.L. Zhang, K. Ikeue, H. Yamashita, M. Anpo, *J. Catal.* 185 (1999) 114.
- [20] J. Peral, D.F. Ollis, *J. Catal.* 136 (1992) 554.
- [21] E. Pellizzetti, C. Minero, *Electrochim. Acta* 38 (1993) 47.
- [22] K. Tanaka, M.F.V. Capule, T. Hisanaga, *Chem. Phys. Lett.* 187 (1991) 73.
- [23] B. Ohtani, Y. Ogawa, S.-I. Nishimoto, *J. Phys. Chem. B* 101 (1997) 3746.
- [24] J.C. Yu, J.G. Yu, W.K. Ho, J.C. Zhao, *J. Photochem. Photobiol. A* 148 (2003) 263.
- [25] R.R. Bacsa, J. Kiwi, *Appl. Catal. B* 16 (1998) 19.
- [26] Q.H. Zhang, L. Gao, J.K. Guo, *Appl. Catal. B* 26 (2000) 207.
- [27] R.M. Alberici, M.C. Canela, M.N. Eberlin, M.F. Jardim, *Appl. Catal. B* 30 (2001) 389.
- [28] L.X. Gao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, *J. Catal.* 196 (2000) 253.
- [29] M.L. Sauer, D.F. Ollis, *J. Catal.* 163 (1996) 215.
- [30] L.A. Dibble, G.B. Raupp, *Catal. Lett.* 4 (1990) 345.
- [31] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223.
- [32] A.J. Maira, J.M. Coronado, V. Augugliaro, K.L. Yeung, J.C. Conesa, J. Soria, *J. Catal.* 202 (2001) 413.
- [33] V. Augugliaro, L. Pacmisano, A. Scalfani, C. Minero, E. Pelizzetti, *Toxicol. Environ. Chem.* 16 (1988) 89.
- [34] L.A. Phillips, G.B. Raupp, *J. Mol. Catal.* 77 (1992) 297.
- [35] J.G. Yu, J.C. Yu, X.J. Zhao, *J. Sol-Gel Sci. Technol.* 24 (2002) 95.
- [36] M.A. Henderson, *Langmuir* 12 (1996) 5093.