Photo-oxidation of gas-phase cyclohexane species over nanostructured TiO₂ fabricated by different strategies

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1. Introduction

Cyclohexane is mainly used in the production of cyclohexanone and cyclohexanol, which are then processed into caprolactam, adipic acid, and subsequently nylon 6 and nylon 66 [1]. Suresh et al. reported that all of the adipic acid and about 63% of the caprolactam produced in the world in 1990 used cyclohexane oxidation as the first step [2]. The amount of cyclohexane oxidized in this way exceeds 4 million tons annually [1]. Moreover, cyclohexane is also used as a solvent in the organic industry. Cyclohexane has a logarithm of the partition coefficient of the given solvent in an equimolar mixture of octanol and water. Compounds with log Pₐₕ values below 4 are considered extremely toxic [3]. Cyclohexane belongs to volatile organic compounds (VOCs). It has been reported that photocatalytic reactions are useful in the treatment of air polluted with VOCs [4]. Thus, detailed investigations on the photocatalytic oxidation of gaseous cyclohexane over various photocatalysts are of great interest.

Among the common photocatalysts, titanium dioxide (TiO₂) is the most promising and suitable material because it is chemical and biological inertness, non-toxicity, non-photo-corrosion, and low cost [5]. TiO₂ is widely used in air cleaning and water purification. Under light irradiation, electrons in the valence band of titanium dioxide are excited to the conduction band and positive holes are left in the valence band. The hole can oxidize the hydroxyl group or water adsorbed on the surface of TiO₂ to form free hydroxyl radical, which is believed to be responsible for the oxidation of pollutants. However, owing to the wide bandgap (for anatase 3.2 eV; ∼390 nm), the utilization of TiO₂ remains confined to UV light. Less than 5% of the solar light energy can be absorbed by TiO₂ [6]. Moreover, the recombination of electron–hole pairs also reduces the photocatalytic activity of TiO₂.

To improve the utilization efficiency of visible light and the photocatalytic quantum efficiency of TiO₂, many modification methods have been developed such as doping with metallic and non-metallic elements, surface acidification, microwave irradiation, and so on. Chen et al. reported that the K⁺-doped TiO₂ (K₄₋ₓTiO₂ with multiple x values) was more photoactive than plain TiO₂ because the recombination of electron–hole pairs was reduced [7]. Beranek and Kisch doped TiO₂ with N by heating TiO₂ film electrode at 400 °C in the presence of urea pyrolysis products [8]. It was found that photocurrent can be observed in the visible down to 700 nm. Wang and Shui prepared PO₄³⁻ and PO₄³⁻–SO₄²⁻ modification of TiO₂ by the method of precipitation-dipping. Their experimental results demonstrated that super acidification of TiO₂ increased its absorbance in ultraviolet region, and improved the photocatalytic activity on 365 nm light [9]. Addamo et al. prepared TiO₂ gels by dialysis of aqueous TiCl₄ solutions. The gels were then thermically treated by a microwave hydrothermal treatment. The use of microwave enhanced the crystallinity of TiO₂ preventing an increase of particle size and minimizing the decrease of specific surface area [10]. These research fruits indicate that through the modification of various methods, TiO₂ with higher photocatalytic activity can be achieved.
In this paper, the commercial TiO₂ photocatalyst Degussa P25 was modified by three facile methods: SO₄²⁻ acidification, SO₄²⁻ acidification combined with microwave irradiation, and microwave irradiation. The decomposition of cyclohexane in gas phase by TiO₂ photocatalyst Degussa P25 and these modified TiO₂ photocatalysts was comparatively investigated. The purpose of this paper is to evaluate the activities of these modified TiO₂ photocatalyst in treating gaseous cyclohexane.

2. Experimental

2.1. Materials

All chemicals were analytical grade and used without further purification. Double deionized water was used. First, 1.0 g of Degussa P25 TiO₂ (labeled as P25) was soaked in H₂SO₄ solution (0.5 mol/L, 10 mL) under constant stirring for 1 h, and then was centrifuged at 20 °C at 10,000 rpm to collect the acidified TiO₂ (labeled as SH). Next, the SH was heated at 100 °C for 24 h and this modified TiO₂ powder was labeled as STH. For the modification method of microwave irradiation combined with SO₄²⁻ acidification, firstly the above-mentioned SH was prepared, and then the SH was irradiated by microwave (700 W, 2450 Hz) for 5 min and this modified TiO₂ powder was labeled as STW. For the modification method of microwave irradiation, 1.0 g of P25 was irradiated by microwave (700 W, 2450 Hz) for 5 min and this modified TiO₂ powder was labeled as WT.

2.2. Characterization

The crystallinity of TiO₂ samples was determined from X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation (Shimadzu Lab-X XRD-6000). The separation characteristics of photogenerated charge carriers were tested by a lock-in-based surface photovoltage spectroscopy (SPS) measurement system. The chemical compositions and structures of P25, WT, STH and STW were determined by a Fourier transform infrared spectrophotometer (Prestige-21, Shimadzu) using KBr pellets.

2.3. Measurement of the photocatalytic properties

The photocatalytic oxidation of cyclohexane in gas phase over P25, WT, STH and STW was investigated using an in-situ quartz infrared photo-reaction cell. The cell (diameter, 4 cm; length, 10 cm) consisted of two NaCl windows and a sample holder (diameter, 13 mm) for the catalyst wafer (Fig. 1). The photocatalyst was illuminated by two 6 W black-light fluorescent lamps with the light intensity of 0.45 mW/cm². The catalyst wafer was prepared by mixing 0.03 g of P25 with 0.17 g of KBr and then through an oil press (80 kN/m²) to produce a flake with 13 mm in diameter. Three wafers were prepared in parallel. The same setup was also used for the wafers of WT, STH and STW.

The compressed air used in the reaction was metered (150 mL/min) and pretreated through three drying columns packed with silica gel, CaCl₂, and molecular sieves, respectively. The reaction cell was purged by the dry air for 1 h. After 1 h, the flux of dry air was set at 35 mL/min. Cyclohexane was fed using a syringe pump to a mixing tee where it was vaporized and mixed with the dry air. The reactant mixture then flowed through the reaction cell and allowed to equilibrate at room temperature (298 K). Once the reactant concentration was stabilized, the inlet and outlet ports were shut off and the lamps were turned on. The initial reactant concentration of cyclohexane was about 38 mg/L. The infrared spectra were continuously collected during the reaction. After 6 h, the lamps were turned off and the cell was purged with flowing dry air. The same operation without lamp irradiation or without photocatalysts was used

Fig. 1. Schematic diagram of the photo-reaction cell. (a) Front view; (b) top view.
as control. The infrared spectra were collected with a resolution of 4 cm\(^{-1}\) and 20 scans in the region of 4000–1000 cm\(^{-1}\).

2.4. Analytic method

The IR spectrum at 2930 cm\(^{-1}\) of cyclohexane was chosen to calculate peak area integral. The degradation percentage of cyclohexane was calculated by Eq. (1):

\[
\eta = \frac{A_0 - A_t}{A_0} \times 100\%
\]

where \(A_0\) is the initial peak area integral and \(A_t\) is the peak area integral after a certain period of illumination time.

3. Results and discussion

3.1. Characterization of P25, WT, STH and STW

3.1.1. FT-IR study

Fig. 2 shows the FT-IR spectra of P25, WT, STH, and STW, respectively. The infrared spectra in the region between 400 cm\(^{-1}\) and 700 cm\(^{-1}\) were assigned to (Ti–O) of TiO\(_2\). The signals at 3440 and 1630 cm\(^{-1}\) were attributed to the adsorbed water on TiO\(_2\). For WT and STW, the intensities of bands 3440 and 1630 cm\(^{-1}\) were less than those of P25 and STH. These results indicated that after the modification of microwave irradiation, the surface coverage of water on TiO\(_2\) decreased. This phenomenon may benefit more reactants attaching to active sites of oxidation on the catalyst surface.

As shown in Fig. 2, the bands located at 1230 cm\(^{-1}\), 1140 cm\(^{-1}\), 1040 cm\(^{-1}\) and 990 cm\(^{-1}\) were observed for STH and STW. In the sulfated metal oxides, the sulfate moiety is covalently bonded to the metal atom. When linked by two oxygen atoms to metal centers, two kinds of coordination modes can be found: chelate or bridged form. The bands at 1230 cm\(^{-1}\) and 1140 cm\(^{-1}\) were ascribed to asymmetric and symmetric stretching of S=O bond, respectively. Also, the bands at 1044 cm\(^{-1}\) and 990 cm\(^{-1}\) were attributed to asymmetric and symmetric stretches of the S–O bond, respectively. Bands of absorption between 900 cm\(^{-1}\) and 1250 cm\(^{-1}\) indicate that SO\(_4^{2-}\) is covalently bonded to Ti\(^{4+}\) in chelate form [11]. Such an interaction is believed to be a driving force in the generation of a large amount of strong Lewis and Bronsted acidic sites on the surface of TiO\(_2\), which can provide better adsorption centers for reactant molecules [12,13].

3.1.2. X-ray diffraction (XRD) study

The XRD images were shown in Fig. 3. The primary crystalline phase of the nanostructured P25, WT, STH, and STW was anatase. Rutile was also present in all the samples. Anatase crystalline TiO\(_2\) is generally accepted to have significant photocatalytic activity [14,15]. The average crystal sizes calculated by Scherrer formula were 14.77 nm, 14.35 nm, 13.39 nm and 13.09 nm corresponded to P25, WT, STH, and STW, respectively. Compared to P25, the crystal sizes of these modified samples decreased.

3.1.3. Surface photovoltage spectroscopy (SPS) study

The SPS method is a well-established technique for the characterization of semiconductors, which provides both optical and transport properties of different regions in the material under study, with high sensitivity to defect states in the sample at its surface, bulk, or any buried interface. The detected response depends on the light absorption, charge separation and transport properties of the sample [16]. Fig. 4 shows the surface photovoltage spectra of P25, WT, STH, and STW. All the samples had an absorption band from 300 nm to 410 nm due to the transition of the O\(_2^−\) antibonding orbital to the lowest empty orbital of Ti\(^{4+}\) [17]. WT, STH and STW exhibited blue shift, which should be caused by their reduced grain sizes after modification, as indicated by the XRD results. Correspondingly, the widened bandgaps will raise the oxidative potential of the photogenerated holes, thus improved photocatalytic activity induced by these modifications is expected.

The electric-field-induced surface photovoltage spectra of P25, WT, STH, and STW were measured as shown in Fig. 5a–d, respectively [18]. For WT, a new response peak at 392 nm appeared when the external positive electrical field was 0.5 V, which is related to charged surface detects. Fig. 5b also shows that the intensity of peak.
392 nm increased with the increase in the external positive electrical field from 0.5 V to 1.0 V. As shown in Fig. 5d, a new response peak at 365 nm of STW emerged on 1.0 V of external positive electrical field. No new response peak was found in P25 and STH. These results demonstrate that the modification of microwave irradiation can result in defect states on the surface of TiO$_2$, which is believed to effectively reduce the recombination of electron–hole pairs and potentially promote the photocatalytic activity [16,19].

3.2. Photocatalytic oxidation of gaseous cyclohexane over P25, WT, STH, and STW

3.2.1. Photocatalytic ability of P25, WT, STH, and STW

As shown in Fig. 4, WT exhibits a very strong photovoltaic response at around 345 nm, indicating that the photo-induced electron–hole pairs in the material are better separated. In general, the photo-induced holes can be easily captured by chemisorbed surface hydroxyl groups to produce hydroxyl radical groups, OH$^•$, while the electrons can be trapped by adsorbed O$_2$ to produce superoxide radicals, O$_2$$^•^-$. Both kinds of radical groups have been shown to be capable of contributing to the oxidation process of organic substances. Moreover, the electric-field-aided SPS study shows that there are more defect states on the surface of WT than that of STW. The improved separation ability of electron–hole pairs

![Fig. 5. EFISPS spectra of TiO$_2$ samples. (a) P25; (b) WT; (c) STH; (d) STW.](image-url)
and more defect states in WT account for its highest photocatalytic activity. These results demonstrate that after the modification of SO$_4^{2-}$ acidification, SO$_4^{2-}$ acidification combined with microwave irradiation, and microwave irradiation, higher photocatalytic ability of TiO$_2$ can be achieved. P25 modified by the microwave irradiation exhibits the highest photocatalytic activity.

3.2.2. In-situ infrared reaction study

In-situ infrared reaction study provides real-time monitoring of transient events which are occurring on the catalyst during the reaction. The information on surface adsorbed species obtained from the in-situ study gives important insight on the reaction mechanisms [20]. In this paper, a set of infrared transmittance spectra obtained during the photocatalytic oxidation of cyclohexane over WT was shown in Fig. 7. The spectra were corrected using the clean P25 as the background. Prior to UV illumination ($t = 0$), the spectrum displayed the characteristic cyclohexane bands at 2930 cm$^{-1}$ and 2860 cm$^{-1}$. Upon irradiation, the intensity of bands 2930 cm$^{-1}$ and 2860 cm$^{-1}$ began to decrease. After 6 h, the degradation percentage of cyclohexane reached to 96.29%. The signal corresponding to CO$_2$ (2360 cm$^{-1}$ and 2340 cm$^{-1}$) and H$_2$O (3440 cm$^{-1}$ and 1630 cm$^{-1}$) increased as the reaction progressed. Carbon monoxide (2160 cm$^{-1}$) was also observed. The photocatalytic oxidation of cyclohexane over P25, STH and STW followed the same path (data not shown). These results show that cyclohexane is mineralized into carbon dioxide and water. Moreover, small amount of CO was produced. These results demonstrate that TiO$_2$ based materials are useful in the photocatalytic oxidation of gaseous cyclohexane. After modification by SO$_4^{2-}$ acidification, SO$_4^{2-}$ acidification combined with microwave irradiation, and microwave irradiation, higher photocatalytic performance can be achieved. And TiO$_2$ modified by microwave irradiation possesses the highest photocatalytic activity because of the additional surface defects induced by the treatment.

4. Conclusions

In summary, TiO$_2$ photocatalyst Degussa P25 was modified by three facile methods: SO$_4^{2-}$ acidification, SO$_4^{2-}$ acidification combined with microwave irradiation, and microwave irradiation, respectively. These TiO$_2$ samples were used as the photocatalysts for the oxidation of gaseous cyclohexane. The photocatalytic activity of these samples to treat cyclohexane followed this order: P25 modified by microwave irradiation > P25 modified by SO$_4^{2-}$ acidification combined with microwave irradiation > P25 modified by SO$_4^{2-}$ acidification > P25. During the photocatalytic oxidation of cyclohexane over these TiO$_2$ samples, cyclohexane was mineralized into carbon dioxide and water. Moreover, small amount of CO was produced. These results demonstrate that TiO$_2$ based materials are useful in the photocatalytic oxidation of gaseous cyclohexane. After modification by SO$_4^{2-}$ acidification, SO$_4^{2-}$ acidification combined with microwave irradiation, and microwave irradiation, higher photocatalytic performance can be achieved. And TiO$_2$ modified by microwave irradiation possesses the highest photocatalytic activity because of the additional surface defects induced by the treatment.

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