

# Photocatalytic degradation of mixed gaseous carbonyl compounds at low level on adsorptive TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst using a fluidized bed reactor

Maolin Zhang<sup>a</sup>, Taicheng An<sup>a,\*</sup>, Jiamo Fu<sup>a,b</sup>, Guoying Sheng<sup>a,b</sup>,  
Xinming Wang<sup>a</sup>, Xiaohong Hu<sup>a</sup>, Xuejun Ding<sup>a</sup>

<sup>a</sup> State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan Street, Guangzhou 510640, PR China

<sup>b</sup> School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200072, PR China

Received 6 July 2005; received in revised form 21 November 2005; accepted 23 November 2005

Available online 18 January 2006

## Abstract

An adsorptive silica-supported titania photocatalyst TiO<sub>2</sub>/SiO<sub>2</sub> was prepared by using nanosized titania (anatase) immobilized on silica gel by the sol–gel technique with the titanium tetra isopropoxide as the main raw material and acetic acid as the acid catalyst. Meanwhile the structure and properties of the TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst were studied by means of many modern analysis techniques such as TEM, XRD, and BET. Gas–solid heterogeneous photocatalytic decomposition of four carbonyl compounds mixture at low concentration levels over ultraviolet irradiated TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst were carried out with high degradation efficiencies in a coaxial triple-cylinder-type fluidized bed photocatalytic reactor, which provided efficient continuous contact of ultraviolet photons, silica-supported titania photocatalyst, and gaseous reactants. Experimental results showed that the photocatalyst had a high adsorption performance and a good photocatalytic activity for four carbonyl compounds mixture. Some factors influencing the photocatalytic decomposition of the mixed carbonyl compounds, i.e. the gas flowrate, relative humidity, concentration of oxygen, and illumination time, were discussed in detail. It is found that the photocatalytic reaction rate of four carbonyl compounds decreased in this order: propionaldehyde, acetone, acetaldehyde and formaldehyde.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Photocatalysis; Adsorptive immobilized photocatalyst; Fluidized bed reactor; Carbonyl compounds; Mixture

## 1. Introduction

Carbonyl compounds are directly discharged into the atmosphere as a primary source from industrial processes, vehicle exhausts, cigarette smoking, cook stoves, building and decorating materials, furnishings and household commodities, and produced as a secondary source from photochemical oxidation of atmospheric hydrocarbons (Possanzini et al., 2002; Baez et al., 2003; Bakeas et al.,

2003). In addition, direct biogenic emission sources also are important sources for carbonyl compounds (Singh et al., 1994). So carbonyl compounds are among the major species of organic pollutants in the atmosphere, and also recognized as the important pollutants in indoor air (Granby et al., 1997; Zhang and Smith, 1999). It is known that carbonyl compounds, in particular, lower-molecular-weight carbonyl compounds such as formaldehyde and acetaldehyde have toxic, for example carcinogenic, mutagenic or teratogenic properties (WHO, 1989; CEPA, 1993; Grimaldi et al., 1998), and therefore their presence in the environment is of great concern with regard to their adverse effects to public health. Thus the removal of

\* Corresponding author. Tel.: +86 20 85291510; fax: +86 20 85290706.  
E-mail address: antc99@gig.ac.cn (T. An).

volatile lower-molecular-weight carbonyl compounds from the atmosphere, especially from indoor air, is of great interest because people spend most of their time indoors, where pollutant concentrations are often higher than that of outdoors (Maroni et al., 1995; Nazaroff and Weschler, 2001).

At present, among most commonly used methods, adsorptions on activate carbon for air cleaning just transfer the organic pollutants from one phase to another, and the absolute toxicity of the substances is still preserved. The heterogeneous catalytic oxidation technologies, for example, automotive exhaust treatments (Armor, 1992) and catalytic incineration (Wang and Lin, 2004), must operate at elevated temperatures. So they have both chemical and economic disadvantages. However, heterogeneous photocatalysis is an alternative method for volatile organic compounds (VOCs) control in indoor air because it not only can function in the condition of ambient temperature and pressure, but also can use the mildest and most prevalent oxidant, molecular oxygen. Heterogeneous photocatalytic purification of gaseous organic pollutants has been studied extensively in the past decade (Dolberg, 1996; Jardim and Alberici, 1997; Kim et al., 2002; Ao et al., 2003). However, to increase the reaction rate of the photocatalytic oxidation in the gas–solid heterogeneous photocatalysis, the reaction system must provide efficient continuous contact of ultraviolet photons, photocatalyst and gaseous reactants. It is believed that fluidized bed photocatalytic reactors are more advantageous than fixed bed photocatalytic reactors because of the good contact of catalyst–light and catalyst–reactants (Lim et al., 2000); therefore, the efficient removal of organic pollutants could be obtained in the fluidized bed reactor containing photocatalyst particles. At the same time, the photocatalytic particles in the fluidized bed reactors are easily charged and discharged, resulting in easily regenerating and reusing the photocatalyst.

In previous studies, some researchers had studied the heterogeneous photocatalysis of single carbonyl compound, such as single formaldehyde (Obee, 1996; Noguchi et al., 1998; Zhang et al., 2001; Shiraishi et al., 2003), acetaldehyde (Sopyan et al., 1996; Falconer and Magrini-Bair, 1998; Ohko et al., 1998; Obuchi et al., 1999; Xu and Shiraiishi, 1999), acetone (Lin and Yu, 1998; Zorn et al., 1999; El-Maazawil et al., 2000; Vorontsov et al., 2000; Choi et al., 2001; Coronado et al., 2003), propionaldehyde (Takeda et al., 1995), in various forms of  $\text{TiO}_2$ , for example particulate  $\text{TiO}_2$  or immobilized  $\text{TiO}_2$  film. But in fact, whether in the indoor or outdoor air, the organic pollutants are the mixture of many carbonyl compounds rather than single one in general. Unfortunately, very few publications to date have described the photocatalytic oxidation process in the presence of multiple composition carbonyl compounds. So the photocatalytic oxidation of mixture composition carbonyl compounds system is a main focus of this research. Moreover, most of carbonyl compounds concentrations are all as low as ppbv level in indoor or outdoor air (Feng et al., 2004), and the photocatalytic decomposition efficiency is very low when the concentrations of organic

pollutants are too low (Toyoda, 2000). But a suitable adsorbent can efficiently concentrate the gaseous pollutants at a low concentration level of ppbv. Thus, the combination of adsorption and oxidative destruction appears to be a promising way to overcome the above-mentioned problems existed in the removal of low concentration level gaseous organic pollutants from air. On the other hand, due to photocatalytically decomposing the desorbed organic pollutants, the adsorbent can be regenerated in situ in the photocatalysis process. In the present paper, therefore, an adsorptive silica-supported titania photocatalyst  $\text{TiO}_2/\text{SiO}_2$  was prepared to concentrate and photocatalytically decompose the multicomponent lower-molecular-weight carbonyl compounds (i.e. formaldehyde, acetaldehyde, acetone, propionaldehyde) with low-level concentrations in an annulus fluidized bed photocatalytic reactor. In the experiment processes, when the contaminated gas circulated through the reactor, the carbonyl compounds in the flow gas was adsorbed first on the  $\text{TiO}_2/\text{SiO}_2$  photocatalyst and then concentrated, while the photocatalyst was continuously exposed to UV light to oxidize photocatalytically the adsorbed carbonyl compounds; as a result, the adsorbent can be continuously regenerated in situ. A detailed discussion was also made of some factors influencing the photocatalytic degradation of the carbonyl compounds, i.e. the gas flow rate, humidity, concentration of oxygen, and illumination time.

## 2. Experimental

### 2.1. Materials and reagents

The silica gel (250–425  $\mu\text{m}$ ) used as the support material was obtained from Kanglin Corp. (China), and the Sep-Pak<sup>®</sup> Silica Gel Cartridges used as the sampling medium were purchased from Waters Corp. (USA). Water used in the experimental was doubly distilled and filtered by Milli-Q. Four carbonyl compounds (formaldehyde, acetaldehyde, acetone and propionaldehyde) employed as model organic compounds are all analytical grade reagents (AR), and purchased from Tianjin Chemical Reagent Co., Inc. (China). Both titanium tetra isopropoxide (Chemical Pure, CP) and glacial acetic acid (AR) were purchased from Shanghai Chemical Reagent Co., Inc. (China). The acetonitrile was HPLC grade and was purchased from Merck (Germany). The 2,4-dinitrophenylhydrazine from Fluka (USA), and the calibration standard (DNPH derivatives of carbonyl compounds) from ChemService (USA).

### 2.2. Preparation of immobilized photocatalyst

In the present study, the silica gel was chosen as a support material by reason that it is transparent to near-UV light, and it has large specific surface area and strong adsorbability, while the  $\text{TiO}_2$  sol–gel solution was used to prepare  $\text{TiO}_2/\text{SiO}_2$  photocatalyst by dipping and coating the silica gel. The sol–gel method reported by Kao and

Yang (1996) was modified as followed: titanium tetra isopropoxide was added dropwise into vigorously stirred acetic acid aqueous solution so as to give a 1:10:40 molar ratio of titanium tetra isopropoxide, acetic acid and water. When the white slurry gradually formed, the resulting slurry was peptized by further for 3 h stirring to give a completely transparent sol solution. Then the sol solution was deposited another 60 h for the coating process. The coated silica gel was dried at 80 °C for 1 h after each dipping step. The procedures for dipping, coating and drying were repeated four times. And then the obtained mixture was calcined at 450 °C for 4 h to obtain an immobilized photocatalyst  $\text{TiO}_2/\text{SiO}_2$ . On the basis of the weight gain of the silica gel, we could calculate that titanium dioxide loaded on silica gel was  $4.7 \text{ g } 100 \text{ g}^{-1}$ .

### 2.3. Experimental apparatus

The experimental equipment used in this study consists of a gas cylinder, a fluidized bed photocatalytic reactor, an oil-free gas circulation pump, a vacuum pump, a vaporizing tube with an injection port, a gas sample reservoir with 15 l volume, and the circulation Teflon tubing. The total volume of the circulation Teflon tubing and sample reservoir is ca. 16 l. The schematic diagram of the experimental set-up is shown in Fig. 1a. The photocatalytic degradation of the mixed reactants was carried out by a circulation reaction process using a coaxial triple-cylinder-type fluidized bed photocatalytic reactor shown in Fig. 1b, where a 125 W high-pressure mercury lamp with a maximum emitting radiation of 365 nm (GGZ125, Shanghai Yaming Lighting CO., Ltd.) as the UV-light source was installed in the internal cylinder made of Pyrex glass (25 mm i.d.  $\times$  115 mm height); The cooling water flows through the jacket between the glass external cylinder and the glass middle cylinder (35 mm i.d.  $\times$  110 mm height) to keep the temperature of the circulation reaction gas and the lamp; and the fluidized bed of  $\text{TiO}_2/\text{SiO}_2$  photocatalyst particles is placed in the reactor cell (ca.  $4.71 \text{ cm}^2$  cross sectional area, 100 mm height) made of the internal Pyrex glass cylinder and the middle glass cylinder, through which the mixed reaction gas circularly flows from bottom to top. Above the gas inlet, an annular fritted glass plate located between the internal cylinder and the middle cylinder is used as a gas distributor and a carrier of photocatalyst particles to provide uniform fluidization of  $\text{TiO}_2/\text{SiO}_2$  photocatalyst.

A Rigaka D/max-1200 diffractometer with the accelerating voltage of 40 kV, emission current of 30 mA and the scanning speed of  $4 \text{ deg min}^{-1}$  was used to determine the phase of prepared photocatalysts. SEM images were collected with a mode LEO1530VP microscope (LEO, Germany) operating at 15.00 kV.

### 2.4. Experimental procedure and analytic methods

For all photocatalytic cases, the fluidized-bed photocatalytic reactor was feed in approximately 5 g of the  $\text{TiO}_2/$

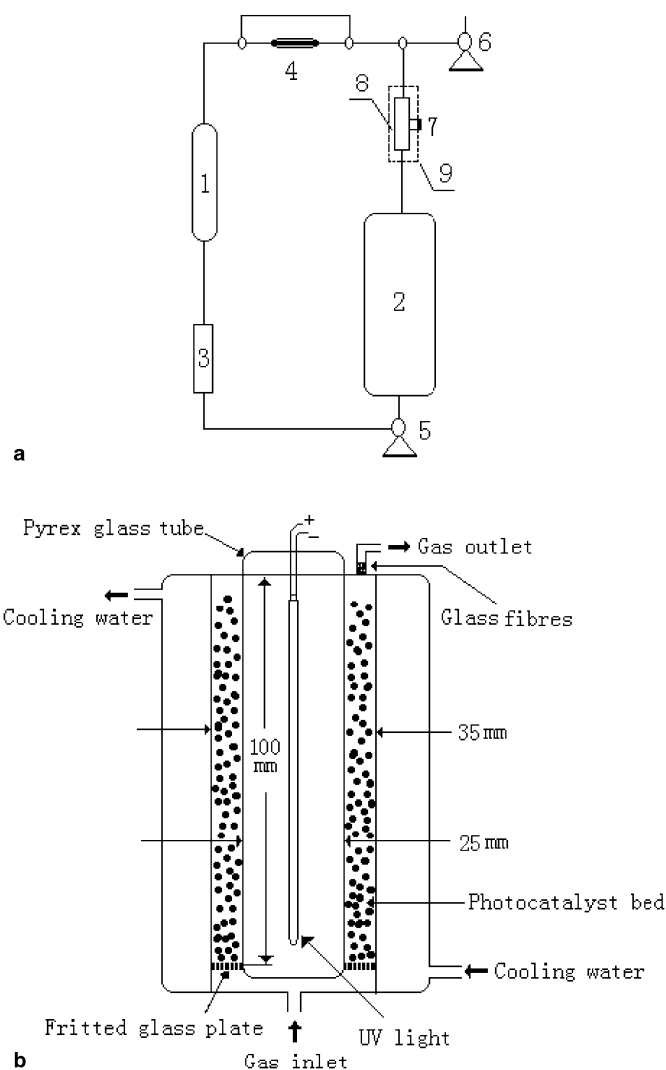


Fig. 1. (a) The schematic diagram of the experimental set-up: 1. photocatalytic reactor (fluidized bed); 2. gas sample reservoir; 3. flowmeter; 4. Sep-Pak<sup>®</sup> silica gel cartridge coated with DNPH; 5. gas circulation pump; 6. vacuum pump; 7. injection port; 8. vaporizing tube; 9. heater. (b) The schematic diagram of the fluidized bed photocatalytic reactor.

$\text{SiO}_2$  photocatalyst, which gave a bed height of ca. 35 mm. The aqueous solution containing four carbonyl compounds were injected into the vaporizing tube through the injection port after the experimental system was washed several times with high purity nitrogen and vacuumed by the vacuum pump. Then they were vaporized by heating the vaporizing tube, and simultaneously,  $\text{O}_2$  and  $\text{N}_2$  from the gas cylinders flow into the vacuumed experimental system until the reaction air pressure equaled to the ambient air pressure. Prior to initiation of photocatalytic degradation, the photocatalyst was forced to achieve gas–solid adsorption equilibrium by circularly flowed the reaction stream. In all tests, the circular gas flowrate through the photocatalysts was  $1.41 \text{ cm s}^{-1}$  except the one for the effect of flowrate and the oxygen concentration in gas stream was ca. 20%  $\text{O}_2$  except the one for the effect of oxygen

concentration, the relative humidity of the gas stream was about 9% except the one for the effect of relative humidity, and the initial concentration of each carbonyl compound was at ca.  $20 \mu\text{mol m}^{-3}$  except the adsorption behavior test of them.

Gas-phase samples were collected by circularly flow the reaction gas through the Sep-Pak<sup>®</sup> Silica Gel Cartridge using a gas circulation pump. A glass ozone scrubber filled with KI was connected to the upstream of the cartridge to remove the interference caused by ozone. After gas-phase sampling, the analysis of the four carbonyl compounds was based on US EPA method TO-11A (US EPA, 1999) and the analytical conditions were based on previous literature (Feng et al., 2004).

### 3. Results and discussion

#### 3.1. Characterization of $\text{TiO}_2/\text{SiO}_2$ supported photocatalyst

Fig. 2 was a plot of XRD pattern from the  $\text{TiO}_2$  powder, the  $\text{TiO}_2/\text{SiO}_2$  and the silica gel under the same experimental condition. The X-ray pattern showed that the  $\text{TiO}_2$  particle calcined at  $450^\circ\text{C}$  was the anatase phase, and the mean crystallite sizes of  $\text{TiO}_2$  were calculated as 15.1 and 5.3 nm for pure  $\text{TiO}_2$  powders and the  $\text{TiO}_2$  in the  $\text{TiO}_2/\text{SiO}_2$  by using the Scherrer formula. Fig. 3 also showed SEM image of the  $\text{TiO}_2/\text{SiO}_2$  and the support, silica gel. It was showed that the  $\text{TiO}_2$  particles were distributed uniformly on silica gel, and the  $\text{TiO}_2$  particle size in  $\text{TiO}_2/\text{SiO}_2$  measured by observing its image was not more than 10 nm, which is smaller than that of the  $\text{TiO}_2$  powder prepared under the identical conditions. This result was also confirmed by the XRD data above. The specific surface area of the silica gel, the  $\text{TiO}_2$  powder and the  $\text{TiO}_2/\text{SiO}_2$  were all measured using a Nova-1000 Surface Area Analyzer (Quantachrome Corporation) with nitrogen as adsorbate, and the values of the silica gel, the  $\text{TiO}_2/\text{SiO}_2$  and the

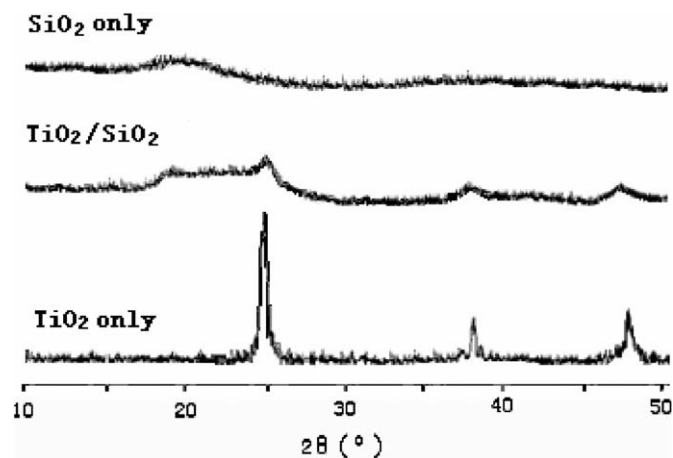


Fig. 2. The XRD pattern of  $\text{SiO}_2$ , prepared  $\text{TiO}_2$  and the supported  $\text{TiO}_2/\text{SiO}_2$ .

$\text{TiO}_2$  powder were ca. 389, 353 and  $82 \text{ m}^2 \text{ g}^{-1}$ , respectively. Thus it was found that the specific surface area of the  $\text{TiO}_2/\text{SiO}_2$  was far larger than that of the  $\text{TiO}_2$  powder, while it just slightly less than that of the silica gel. So we could conclude that, compared with the  $\text{TiO}_2$  powders, the immobilized photocatalyst  $\text{TiO}_2/\text{SiO}_2$  may have an more excellent adsorptive performance for lower concentration organic pollutants in air, and this was confirmed by adsorption tests below.

In order to understand the UV light utilizations efficiency of prepared  $\text{TiO}_2/\text{SiO}_2$  supported photocatalyst, the UV absorption data of the silica gel, the  $\text{TiO}_2/\text{SiO}_2$  and the  $\text{TiO}_2$  powder in suspended aqueous solution were also measured, and the profiles are shown in Fig. 4. From the figure we can find that the silica gel has no apparent adsorption in the range of 200–800 nm, while the  $\text{TiO}_2$  has a significant adsorption peak around 330 nm. However, after the nanometer  $\text{TiO}_2$  was supported onto the silica gel, the UV–VIS adsorption spectrum indicated that the

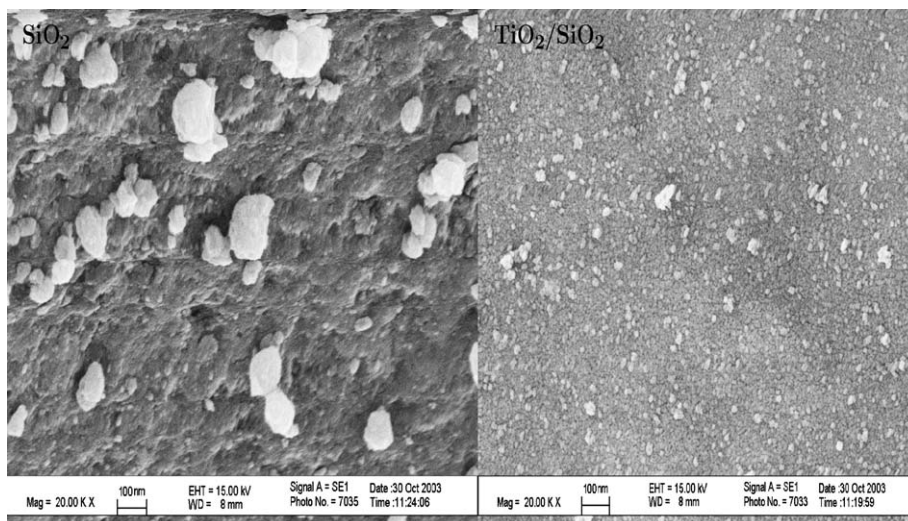


Fig. 3. The SEM photographs of the silica gel with or without supported by  $\text{TiO}_2$ .

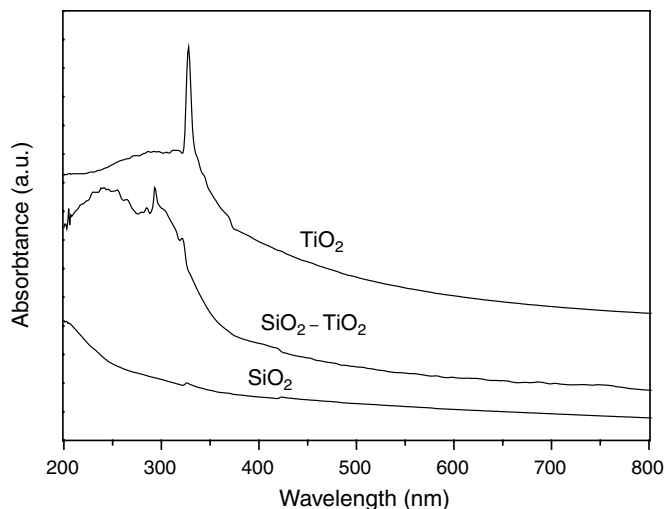


Fig. 4. UV absorption profiles of  $\text{SiO}_2$ , prepared  $\text{TiO}_2$  and the supported  $\text{TiO}_2/\text{SiO}_2$ .

maximum adsorption wavelengths are around 255 and 293 nm. The significant blue-shift of maximum adsorption wavelengths of  $\text{TiO}_2$  particle in  $\text{TiO}_2/\text{SiO}_2$  may be indicated that there exists an apparent nanometer size effect. That is, the smaller of size of  $\text{TiO}_2$ , the more of blue-shift of maximum adsorption wavelengths of  $\text{TiO}_2$  particle. And it is proved again that the  $\text{TiO}_2$  particle size in  $\text{TiO}_2/\text{SiO}_2$  has smaller size than that of the  $\text{TiO}_2$  powder. This conclusion also accords with the result obtained from XRD.

### 3.2. Adsorption behavior of mixed carbonyl compounds

The adsorption of pollutants onto the photocatalyst surface is the first step of photocatalytic reaction; moreover, the adsorbability of the pollutants on the photocatalyst surface is an important factor to influence the photocatalytic degradation efficiency of pollutants (Lu, 1999). Thus, in the present study, the adsorptions of four carbonyl compounds have been performed simultaneously in the presence of the  $\text{TiO}_2/\text{SiO}_2$  photocatalyst. The synthesized gas containing each carbonyl compound of  $30 \mu\text{mol}$  was recirculated through the fluidized bed photocatalyst until the adsorption equilibrium of the carbonyl compounds in circular reaction gas onto the photocatalyst was reached. And their adsorption capacity and the amount of adsorbed molecules per unit surface area on the  $\text{TiO}_2/\text{SiO}_2$  are shown in Fig. 5. Contrastively, the adsorption test of the  $\text{TiO}_2$  powder, which was prepared under the same experimental condition as the  $\text{TiO}_2/\text{SiO}_2$ , and the support  $\text{SiO}_2$  were also performed, and the experimental results are also plotted in Fig. 5. From Fig. 5, it was found that  $\text{TiO}_2/\text{SiO}_2$  had a more excellent adsorptive performance in comparison to the  $\text{TiO}_2$  powder though the amount of adsorbed molecules per square centimeter surface on the  $\text{TiO}_2/\text{SiO}_2$  was less than that on the  $\text{TiO}_2$  powder. However, the adsorption behavior of mixed carbonyl compounds on the support

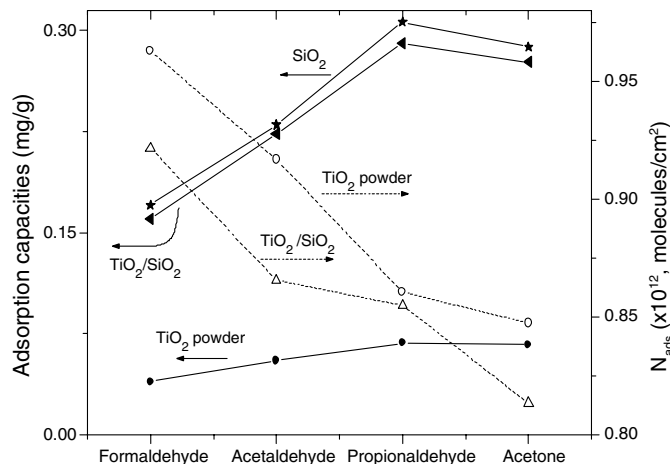


Fig. 5. The adsorption capacities of four carbonyl compounds on the photocatalyst.

$\text{SiO}_2$  was similar to that on the  $\text{TiO}_2/\text{SiO}_2$ , although the adsorption amount of mixed carbonyl compounds on the  $\text{SiO}_2$  was slightly larger than that on the  $\text{TiO}_2/\text{SiO}_2$ . This represented that the pore of silica-gel support was slightly plugged by the immobilized  $\text{TiO}_2$ , which was accordant with the BET surface areas of silica-gel and silica- $\text{TiO}_2$ . Moreover, the adsorbed molecule amounts of the four carbonyl compounds on the  $\text{TiO}_2/\text{SiO}_2$  and the  $\text{TiO}_2$  powder were also found to be increasing in the following trend: acetone, propionaldehyde, acetaldehyde and formaldehyde. According to previous study (El-Maazawil et al., 2000), the saturation coverage of acetone on  $\text{TiO}_2$  surface was  $10^{15}$  molecules per  $\text{cm}^2$ . However, under the present condition, the adsorbed amount of four carbonyl compounds (ca.  $10^{12}$  molecules per  $\text{cm}^2$ ) on the surface of  $\text{TiO}_2/\text{SiO}_2$  is greatly lower than the saturation coverage, so the available adsorption sites on the photocatalyst surface should be over much, and the competition of four carbonyl compounds for adsorption sites on the photocatalyst surface should be only slight. The different adsorbed molecule amounts of four carbonyl compounds on the photocatalyst surface could be explained by the physical and chemical properties of these compounds (i.e., polarizability, dipole moment, electron donation, acid base interaction), which dominated the affinity and the adsorption/desorption rate of them for the catalyst surface. The carbonyl group was the active function group of the carbonyl compounds and should mainly contribute to the affinity of carbonyl compounds for the photocatalyst surface. The carbonyl group in formaldehyde was the most active and was strongly polarized compared with others, so the formaldehyde's affinity for the catalyst surface should be the highest, and the adsorbed amount of formaldehyde on the photocatalyst surface was the most. In addition, the space structure of carbonyl compounds should also be taken into consideration, and the space resistance of carbonyl compounds may also contribute to the adsorbed amount of them on the catalyst surface.

### 3.3. Photolytic and photocatalytic experiments

The photolytic experiments of the four low-level carbonyl compounds was carried out in the absence of the photocatalyst, and the dependence of the irradiation time and the concentrations of the four carbonyl compounds in the reaction system are represented in Fig. 6a. From Fig. 6a, it was found that only a little carbonyl compounds were photolyzed, and the photolytic efficiency is less than 1% for the four all carbonyl compounds after 2 h irradiation; especially, the photolytic efficiency is also less than 1% for acetone after 5 h irradiation. Therefore, it indicated that in the present experimental conditions, the four carbonyl compounds could not be effectively decomposed by the UV light of 365 nm alone, but the photolytic degradation efficiencies of the four carbonyl compounds were found to be increasing in the following trend: acetone, propionaldehyde, acetaldehyde and formaldehyde.

In the presence of  $\text{TiO}_2/\text{SiO}_2$  photocatalyst, the relationship between the reaction time and the concentration of the four carbonyl compounds is plotted in Fig. 6b. In contrast, a dark control experiment also was performed, but the results showed that four carbonyl compounds were not almost degraded under the dark condition. From Fig. 6b, it was found that the four carbonyl compounds could be photocatalytically degraded effectively, and the photocatalytic degradation efficiencies of four carbonyl compounds were all high than 99% within 4 h. It is obvious that propionaldehyde and acetone were more easily degraded than acetaldehyde and formaldehyde, and the degradation efficiencies were both above 99% within 2 h. From the data in Fig. 6b, the linear plot of  $\ln(C_0/C)$  versus irradiation time

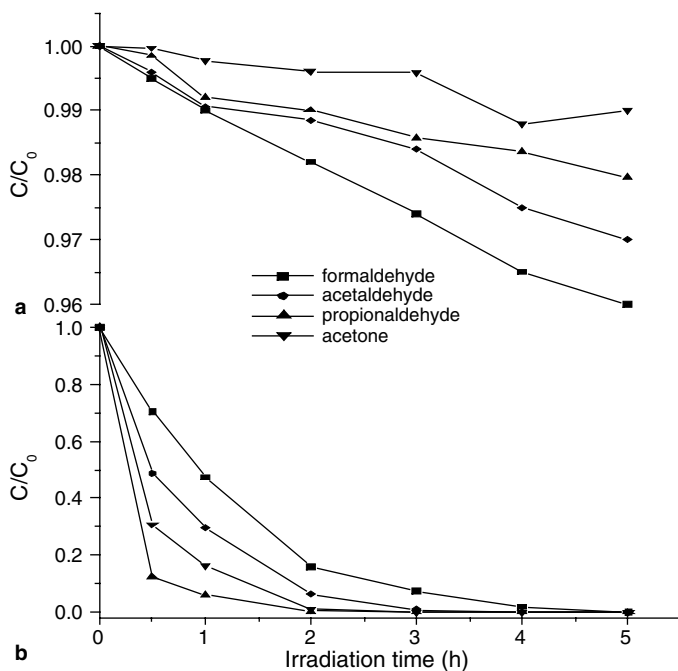


Fig. 6. The photolysis (a) and photocatalytic degradation (b) kinetics of four carbonyl compounds.

could be obtained. Thus, we can conclude that, under the present experimental conditions, the photocatalytic degradation of the four carbonyl compounds all accord with the first-order kinetics. This linear plot also presented the apparent rate constants were 2.34, 2.31, 1.63, and  $1.12 \text{ h}^{-1}$  for propionaldehyde, acetone, acetaldehyde and formaldehyde, respectively. Unexpectedly, this reaction rate trend was not consistent with the adsorption trend of the four carbonyl compounds on the  $\text{TiO}_2/\text{SiO}_2$ . But under the same experimental condition, the apparent rate constants of each single carbonyl compound were 2.47, 2.44, 2.33, and  $2.10 \text{ h}^{-1}$  for propionaldehyde, acetone, acetaldehyde and formaldehyde, respectively. Clearly, the apparent rate constants for single compound degradation were all higher than that of simultaneous degradation of four carbonyl compounds. In case of mixed carbonyl compounds photocatalysis, the reasons about their reaction rate trend now were not clear, and we would study it further in the future works. In the previous study, Sauer and Ollis (1996) reported that formaldehyde was a significant intermediate during the photocatalyzed oxidation of acetaldehyde, so the photocatalyzed degradation of propionaldehyde and acetone may also produce formaldehyde intermediates, which resulted in the low apparent rate constants of formaldehyde. In addition, the high affinity of formaldehyde may make it tightly to integrate with the photocatalyst surface, which also led to its low apparent rate constants.

In order to distinguish photocatalytic degradation effect from adsorption effect, the recoveries of reactants, four carbonyl compounds, were conducted after the reactants' adsorption equilibriums were reached. The recovery percentages were obtained as 99%, 98%, 97% and 97% for carbonyl compounds, formaldehyde, acetaldehyde, acetone and propionaldehyde, respectively. It indicated that although the reactants can adsorb onto the photocatalyst easily, for example 89% formaldehyde, the reactants could completely desorb from the surface of photocatalysts after 2 h recovery experiments. From these data, we can conclude that the degradation efficiencies of four reactants were all valid. Moreover, the adsorptions of reactants onto photocatalysts can increase the rate of surface catalytic degradation reaction of VOCs at the surface of photocatalysts.

### 3.4. The effect of oxygen concentration

It is well known that oxygen is an effective conduction band electron acceptor. Molecular oxygen preadsorbed onto the surface of the photocatalyst can instantly trap the interfacial electron of the photocatalyst so as to suppress the electrons and holes recombination. At the same time, oxygen was reduced by the conduction band electron to form  $\text{O}_2^-$  negative ion, which was further transformed into the OH radical, and the radical is a main oxidant in a photocatalytic process. Therefore, oxygen is necessary and beneficial to the photocatalytic degradation of gaseous pollutants. In the present experiment, the effect of oxygen

concentration at the reaction gas stream on the photocatalytic degradation of four carbonyl compounds was investigated by adjusting the oxygen concentrations from 0% to 100% O<sub>2</sub>, and the dependence of photocatalytic degradation efficiencies of the four carbonyl compounds on the oxygen concentration is shown in Fig. 7a. The experimental results showed that the photocatalytic degradation of the four carbonyl compounds was ineffective without molecular oxygen in the gas stream, and then photocatalytic degradation efficiencies increased quickly with the increasing oxygen concentration. But the photocatalytic degradation efficiencies leveled off gradually when oxygen concentration was over 30%. This experimental phenomenon was mainly interpreted as follow: The valence band holes reacted much faster with organic species than the

conduction band electrons do with oxygen, so the rate of oxygen reduction by the conduction band electron was usually the rate-limiting step in a photocatalytic process, and the photocatalytic degradation rates of carbonyl compounds would increase with the increasing oxygen concentration on the photocatalyst surface. However, oxygen concentration on the photocatalyst surface increased with the increasing oxygen concentration in reaction gas bulk. Therefore, the photocatalytic degradation rates of the four carbonyl compounds also increased with increasing oxygen concentration in reaction gas bulk. But the oxygen concentration on photocatalyst surface would become a saturation value when the oxygen in reaction gas bulk reached certain high concentration. As a result, the photocatalytic degradation rate of carbonyl compounds did not increase with the increasing oxygen concentration in bulk.

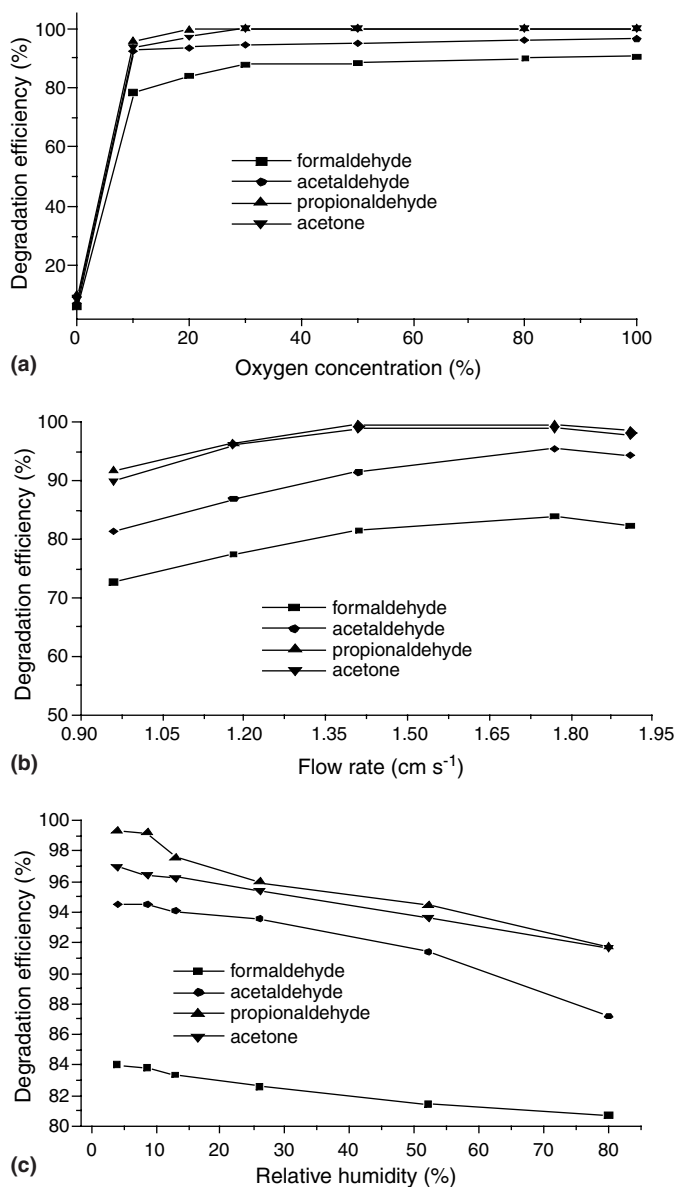


Fig. 7. Effects of the oxygen concentration (a), the flowrate (b) and the humidity (c) on the photocatalytic efficiencies of four carbonyl compounds.

### 3.5. The effect of flowrate

In the gas–solid heterogeneous photocatalysis, the mass transfer resistance from the gas bulk phase to the solid photocatalyst surface would reduce the reaction rate. However, the mass transfer resistance would decrease with increasing the gas flowrate, thus the gas flowrate may be an important factor for a fluidized bed photocatalytic reactor. In this photocatalytic reactor, the minimum fluidization velocity ( $U_{mf}$ ) and terminal velocity ( $U_t$ ) of TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst were calculated as ca. 0.77 cm s<sup>-1</sup> and 78.93 cm s<sup>-1</sup>, respectively. However, in the present study, with variation of the flowrate (0.96–1.91 cm s<sup>-1</sup>), the photocatalytic degradation of the four carbonyl compounds was also carried out, and the photocatalytic degradation efficiencies of the four carbonyl compounds under different flowrates are shown in Fig. 7b. From Fig. 7b, it is found that the photocatalytic degradation efficiencies increased with increasing the flowrate until 1.77 cm s<sup>-1</sup> for formaldehyde and acetaldehyde, 1.41 cm s<sup>-1</sup> for propionaldehyde and acetone. The experimental results showed that the photocatalytic reaction efficiencies of four carbonyl compounds over the TiO<sub>2</sub>/SiO<sub>2</sub> all exhibited maximum values at certain flowrate. This is interpreted that, at optimal flowrate, the contact of photocatalyst, UV light and reactants seemed to be at the optimal condition, and the mass transfer resistance may be also very little. But, further increasing the flowrate, the larger bubbles were formed in the fluidized bed, which decreased the contact of photocatalyst, UV light and reactants. At the same time, the residence time of reactants in the photocatalyst surface was also reduced. Therefore, above the optimal flowrate, the photocatalytic degradation efficiencies of four carbonyl compounds decreased with the increase of flowrate.

### 3.6. The effect of relative humidity

It was known that water vapor plays an important role in the photocatalytic degradation of gaseous organic compounds, and many researchers have investigated the effect

of water vapor on the photocatalytic degradation of gaseous reactants (Huang and Mariñas, 1997). In the present experiment, the photocatalytic degradation reactions of mixed carbonyl compounds were also conducted within the range of relative humidity from about 4% to 80%. Fig. 7c showed that the photocatalytic degradation efficiencies of the four carbonyl compounds all decreased with increasing relative humidity. But the photocatalytic degradation efficiencies of the four carbonyl compounds all decreased slightly with the increase of relative humidity within lower humidity range, and yet decreased apparently with the increase of relative humidity in higher range. This experimental result may be due to the competitive adsorption between water molecules and the carbonyl compounds molecules on the photocatalyst surface, and the masking of moisture on the active sites of the photocatalyst surface.

#### 4. Conclusions

The TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst was a good adsorptive photocatalyst for degrading low-level carbonyl compounds, and the adsorption capacity of the TiO<sub>2</sub>/SiO<sub>2</sub> was approximately four times as large as that of the TiO<sub>2</sub> powder. The high degradation rate of four low-level carbonyl compounds achieved using the TiO<sub>2</sub>/SiO<sub>2</sub> prepared in this study, and the photocatalytic degradation of four carbonyl compounds in the fluidized bed photocatalytic reactor all accord with the first-order kinetics. Moreover, the photocatalytic reaction rates of four carbonyl compounds were found to be decreased in the following trendy: propionaldehyde, acetone, acetaldehyde and formaldehyde.

#### Acknowledgement

The authors are grateful to Dr. Yanli Feng, and Prof. Guangxin Wang for their assistance in the experiments. Thanks also give to the financial support from The National Nature Science Foundation of China (No. 40572173), The Sci. & Technol. Project of Guangdong province, China (No. 2005A30401001), The Nature Science Foundation of Guangdong province, China (No. 04002146), and China Postdoctoral Science Foundation (No. 2004036018).

The authors also want to express thanks to the editor and the anonymous reviewers for their valuable comments to the manuscript.

#### References

Ao, C.H., Lee, S.C., Mak, C.L., Chan, L.Y., 2003. Photodegradation of volatile organic compounds (VOCs) and NO for indoor air purification using TiO<sub>2</sub>: promotion versus inhibition effect of NO. *Appl. Catal. B: Environ.* 42, 119–129.

Armor, J.N., 1992. Environmental catalysis. *Appl. Catal. B: Environ.* 1, 221–256.

Baez, A., Padilla, Garcia, H.R., Torres, M.C., Rosas, I., Belmont, R., 2003. Carbonyl levels in indoor and outdoor air in Mexico City and Xalapa, Mexico. *Sci. Total Environ.* 302, 211–226.

Bakeas, E.B., Argyris, D.I., Siskos, P.A., 2003. Carbonyl compounds in the urban environment of Athens, Greece. *Chemosphere* 52, 805–813.

CEPA (California Environmental Protection Agency), 1993. Acetaldehyde as a toxic air contaminant, Part A: exposure; Part B: health assessment. Air Resources Board, Stationary Source Division, Sacramento, CA, USA.

Choi, W., Ko, J.Y., Park, H., Chung, J.S., 2001. Investigation on TiO<sub>2</sub>-coated optical fibers for gas-phase photocatalytic oxidation of acetone. *Appl. Catal. B: Environ.* 31, 209–220.

Coronado, J.M., Zorn, M.E., Tejedor-Tejedor, I., Anderson, M.A., 2003. Photocatalytic oxidation of ketones in the gas phase over TiO<sub>2</sub> thin films: a kinetic study on the influence of water vapor. *Appl. Catal. B: Environ.* 43, 329–344.

Dolberg, S.K., 1996. Heterogeneous photocatalysis for control of volatile organic compounds in indoor Air. *J. Air Waste Manag. Assoc.* 46, 891–898.

El-Maazawil, M., Finken, A.N., Nair, A.B., Grassian, V.H., 2000. Adsorption and photocatalytic oxidation of acetone on TiO<sub>2</sub>: an in situ transmission FT-IR study. *J. Catal.* 191, 138–146.

Falconer, J.L., Magrini-Bair, K.A., 1998. Photocatalytic and Thermal Catalytic Oxidation of Acetaldehyde on Pt/TiO<sub>2</sub>. *J. Catal.* 179, 171–178.

Feng, Y.L., Wen, S., Wang, X.M., Sheng, G.Y., He, Q.S., Tang, J.H., Fu, J.M., 2004. Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China. *Atmos. Environ.* 38, 103–112.

Granby, K., Christensen, C.S., Lohse, C., 1997. Urban and semi-rural observations of carboxylic acids and carbonyls. *Atmos. Environ.* 31, 1403–1415.

Grimaldi, F., Taibi, R., Bongrand, P., Timon-David, P., Viala, A., 1998. Risk assessment of exposure to aldehydic compounds in a hospital environment. *Toxicol. Lett.* 95 (Suppl. 1), 222–228.

Huang, C.H., Mariñas, B.J., 1997. Role of water in the photocatalytic degradation of trichloroethylene vapor on TiO<sub>2</sub> films. *Environ. Sci. Technol.* 31, 1440–1445.

Jardim, W.F., Alberici, R.M., 1997. Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide. *Appl. Catal. B: Environ.* 14, 55–68.

Kao, C.F., Yang, W.D., 1996. Preparation and electrical characterisation of strontium titanate ceramic from titanil acylate precursor in strong alkaline solution. *Ceram. Inter.* 22, 57–66.

Kim, S.B., Hwang, H.T., Hong, S.C., 2002. Photocatalytic degradation of volatile organic compounds at the gas–solid interface of a TiO<sub>2</sub> photocatalyst. *Chemosphere* 48, 437–444.

Lim, T.H., Jeong, S.M., Kim, S.D., Gyenis, J., 2000. Photocatalytic decomposition of NO by TiO<sub>2</sub> particles. *J. Photochem. Photobiol. A: Chem.* 134, 209–217.

Lin, J., Yu, J.C., 1998. An investigation on photocatalytic activities of mixed TiO<sub>2</sub>-rare earth oxides for the oxidation of acetone in air. *J. Photochem. Photobiol. A: Chem.* 116, 63–67.

Lu, M.C., 1999. Photocatalytic oxidation of propoxur insecticide with titanium dioxide supported on activated carbon. *J. Environ. Sci. Health. B* 34, 207–223.

Maroni, M., Seifert, B., Lindvall, T., 1995. *Indoor Air Quality—A Comprehensive Reference Book*. Elsevier, Amsterdam.

Nazaroff, W.W., Weschler, C.J., 2001. Indoor air and the public good. *Indoor Air* 11, 143–144.

Noguchi, T., Fujishima, A., Sawunyama, P., Hashimoto, K., 1998. Photocatalytic degradation of gaseous formaldehyde using TiO<sub>2</sub> film. *Environ. Sci. Technol.* 32, 3831–3833.

Obee, T.N., 1996. Photooxidation of sub-parts-per-million toluene and formaldehyde levels on titania using a glass-plate reactor. *Environ. Sci. Technol.* 30, 3578–3584.

Obuchi, E., Sakamoto, T., Nakano, K., Shiraishi, F., 1999. Photocatalytic decomposition of acetaldehyde over TiO<sub>2</sub>/SiO<sub>2</sub> catalyst. *Chem. Eng. Sci.* 54, 1525–1530.

Ohko, Y., Tryk, D.A., Hashimoto, K., Fujishima, A., 1998. Autoxidation of acetaldehyde initiated by TiO<sub>2</sub> photocatalysis under weak UV illumination. *J. Phys. Chem. B* 102, 2699–2704.



- Possanzini, M., Palo, V.D., Cecinato, A., 2002. Sources and photodecomposition of formaldehyde and acetaldehyde in Rome ambient air. *Atmos. Environ.* 36, 3195–3201.
- Sauer, M.L., Ollis, D.F., 1996. Photocatalyzed oxidation of ethanol and acetaldehyde in humidified air. *J. Catal.* 158, 570–582.
- Shiraishi, F., Yamaguchi, S., Ohbuchi, Y., 2003. A rapid treatment of formaldehyde in a highly tight room using a photocatalytic reactor combined with a continuous adsorption and desorption apparatus. *Chem. Eng. Sci.* 58, 929–934.
- Singh, H.B., O'Hara, D., Herlth, D., Sachse, W., Blake, D.R., Bradshaw, J.D., Kanakidou, M., Crutzen, P.J., 1994. Acetone in the atmosphere: distribution, sources, and sinks. *J. Geophys. Res.* 99, 1805–1819.
- Sopyan, I., Watanabe, M., Murasawa, S., Hashimoto, K., Fujishima, A., 1996. An efficient TiO<sub>2</sub> thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation. *J. Photochem. Photobiol. A: Chem.* 98, 79–86.
- Takeda, N., Torimoto, T., Sampath, S., Kuwabata, S., Yoneyama, H., 1995. Effect of inert supports for titanium dioxide loading on enhancement of photodecomposition rate of gaseous propionaldehyde. *J. Phys. Chem.* 99, 9986–9991.
- Toyoda, K., 2000. A Study on the Photocatalytic Decomposition of Volatile Organic Compounds in a Closed Ecological System. Master's thesis, Kyushu Institute of Technology.
- US EPA, 1999. Compendium method TO-11A, Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [active sampling methodology].
- Vorontsov, A.V., Savinov, E.N., Smirniotis, P.G., 2000. Vibrofluidized- and fixed-bed photocatalytic reactors: case of gaseous acetone photo-oxidation. *Chem. Eng. Sci.* 55, 5089–5098.
- Wang, C.H., Lin, S.S., 2004. Preparing an active cerium oxide catalyst for the catalytic incineration of aromatic hydrocarbons. *Appl. Catal. A: General* 268, 227–233.
- WHO (World Health Organization), 1989. Environmental Health Criteria 89, Formaldehyde, WHO, Geneva.
- Xu, J.H., Shiraishi, F., 1999. Photocatalytic decomposition of acetaldehyde in air over titanium dioxide. *J. Chem. Technol. Biotechnol.* 74, 1096–1100.
- Zhang, J., Smith, K.R., 1999. Emissions of carbonyl compounds from various cookstoves in China. *Environ. Sci. Technol.* 33, 2311–2320.
- Zhang, Y., Xiong, G., Yao, Yang, W., Fu, X., 2001. Preparation of titania-based catalysts for formaldehyde photocatalytic oxidation from TiCl<sub>4</sub> by the sol-gel method. *Catal. Today* 68, 89–95.
- Zorn, M.E., Tompkins, D.T., Zeltner, W.A., Anderson, M.A., 1999. Photocatalytic oxidation of acetone vapor on TiO<sub>2</sub>/ZrO<sub>2</sub> thin films. *Appl. Catal. B: Environ.* 23, 1–8.