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Benz[a]anthracene Heterogeneous Photochemical Reaction on the Surface of TiO₂ Particles

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Abstract: The photochemical reaction of benz[a]anthracene (B[a]A) on TiO₂ particles was investigated by using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and gas chromatography-mass spectrometry (GC-MS). It was confirmed that photocatalytic oxidation of benz[a]anthracene occurred on the surface of TiO₂ particles, and surface hydroxyl and surface oxygen participated in the reactions. The main photochemical product of benz[a]anthracene was benz[a]anthracene-7,12-dione. Possible photochemical mechanism of benz[a]anthracene was also proposed. Under the simulated sunlight irradiation (22 mW·cm^{-2}), the process of benz[a]anthracene photodegradation on TiO₂ particles matched the exponential decay equation, and the half-life time was 6.8 min.

Key Words: Benz[a]anthracene; TiO₂; Photochemical reaction; DRIFTS

Polycyclic aromatic hydrocarbons (PAHs), an important class of pollutants, are ubiquitously distributed in the environment, possessing mutagenic, carcinogenic, and teratogenic properties[1]. In atmosphere, they are adsorbed principally on the particulate matter, and they prove to be a real threat to human health once they enter the human body. The photochemical reaction of PAHs at atmospheric particulate/gas interface has been shown to play a key role in the transformation of these pollutants in the environment. PAHs photodegradation rate and pathway are liable to be strongly influenced by different atmospheric particulate substrates on which they are adsorbed; therefore, it has been the focus of much study.

Previous studies on the mechanism of photochemical oxidation of PAHs absorbed on particulate matter have mainly focused on insulator particulate relative abundance in atmosphere, such as SiO₂, Al₂O₃, and fly ash[2−6]. Fioressi *et al.*[2] studied the photochemical reaction of benzo[a]pyrene on silica gel and alumina surfaces with the help of a 1000 W Xe lamp; Reyes *et al.*[3] studied the photochemical reaction of pyrene on unactivated and activated silica surfaces; Behymer *et al.*[4] studied the photochemical reaction of benz[a]anthracene on

SiO₂, Al₂O₃, and fly ash. There are at least four different possible initiation processes of PAH photodegradation: (1) direct energy transfer from a photosensitizer to the PAH, (2) formation of singlet oxygen, (3) free radical chain reactions initiated by the excited state PAHs, and (4) hydrogen abstraction by other excited state species, leading to radical chain reactions that involve PAHs[2,3,7].

The tropospheric aerosols contain semiconductor oxide photocatalysts like TiO₂ and Fe₂O₃, besides insulator oxides. When a semiconductor particle absorbs a light quantum with an energy that exceeds its band gap, an electron from the valence band is excited into the conduction band, and then participates in the atmospheric photochemical reaction[8]. However, few studies investigated the atmospheric photochemical reaction of PAHs at the semiconductor particulate/gas interface.

In this study, the semiconductor oxide TiO₂, which is present in troposphere aerosols in comparatively medium amounts (Ti concentrations estimated to be in the range of 50−100 ng·m^{-3} [3]), and benz[a]anthracene, one of the sixteen PAHs classified by US EPA as priority pollutants, were cho-

sen as the research subject. The photochemical reaction of benz[a]anthracene on TiO_2 particles was investigated by using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and gas chromatography-mass spectrometry (GC-MS). The mechanism of the photochemical reaction of benz[a]anthracene on TiO_2 particles was proposed and preliminary kinetic results were obtained.

1　Experimental

1.1　Samples and reagents

Benz[a]anthracene (98%) was purchased from Fluka Chemical Company, USA. P25 TiO_2 (99.5%) was kindly supplied by Degussa Co., Germany. Methanol (99.7%) was purchased from Shanghai Chemical Reagent Research Institute, China. Residue grade dichloromethane (99.8%) was purchased from Sigma-Aldrich Laboratory (Milwaukee, WI, USA). High purity (99.999%) He, Ar, and CO_2 were obtained from Shanghai Yunguang Company, China. High purity (99.999%) O_2 was obtained from Shanghai Pujiang Company, China.

1.2　Experimental apparatus

The *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) photochemical reaction system was similar to the reaction system reported by Vogt *et al.*[9]. It was composed of the following instruments: a FTIR spectrometer (Nicolet AVATAR 380) equipped with a high-sensitivity MCT detector, cooled by liquid N_2, the corresponding accessories were the "Praying Mantis" (Harrick) system of mirrors for collecting the diffuse IR radiation and a low temperature environmental chamber (Harrick Model CHC-CHA-3). The chamber temperature was controlled by an electronic controller (Harrick Model ATC-024-2). The radiant light was obtained by a 500 W xenon lamp (Beijing TrusTech Science and Technology Co., China) equipped with a quartz lens (diameter 5 mm). The radiant flux was measured with a photometer (International Light Model IL1400A).

Reaction products were analyzed by gas chromatography-mass spectrometry using a 6890 gas chromatograph/5973N mass spectrometry (Agilent, USA). Supercritical Fluid Extraction (SFE) was performed with a SFX^{TM} 220 SFE System (Isco Inc., USA) using high purity CO_2.

1.3　Experimental methods

1.3.1　Preparation of samples

Preadsorption of benz[a]anthracene on TiO_2 (B[a]A/TiO_2) was carried out as follows: 25 mg of benz[a]anthracene was added to 50 mL methanol. Then 500 mg TiO_2 was added after the benz[a]anthracene dissolved in the methanol. At last the suspension was stirred in the dark until the methanol volatilized completely.

1.3.2　Photochemical experiments

The photocatalytic oxidation of benz[a]anthracene on TiO_2 was studied in the photochemical reaction system by DRIFTS. 50 mg of B[a]A/TiO_2 was held in the sample cell of the chamber, and the sample cell temperature was controlled at (25±1) ℃. Irradiation of the samples was carried out by an Xe lamp passing through the quartz windows, and at the same time the infrared spectra were collected. The infrared spectra were typically recorded in the 4000−650 cm^{-1} spectra region with 4 cm^{-1} resolution for 64 scans. The background spectrum was collected in the dark, placing pure TiO_2 in the sample cell. During the photochemical reaction, the gas inlet and outlet of the reactor were closed. The reaction atmosphere was air, with no special indication. To investigate the effect of different irradiation wavelengths on the photochemical reaction, different cutoff filters ($\lambda>350$ nm, $\lambda>450$ nm) were used to obtain the desired irradiation. When the light irradiated on the surface of the sample directly, the light intensity was 1.2 $mW·cm^{-2}$, the light intensity was 0.7 $mW·cm^{-2}$ through the 450 nm cutoff filter, and the light intensity was 0.9 $mW·cm^{-2}$ through the 350 nm cutoff filter.

1.3.3　Surface products analysis

The identification of photochemical products on the TiO_2 particles was carried out by GC-MS after supercritical fluid extraction (SFE). SFE was carried out by the following procedure: a 10-min period on static mode, followed by 30-min dynamic extraction at 80 ℃ and 26.8 MPa. Supercritical fluid flow rate on dynamic step was held at 1.5 $mL·min^{-1}$ by a variable-flow restrictor, adding 5% methanol as additive. Collection of the extracted analyte was carried out in a test tube filled with dichloromethane. The analysis was performed on a GC-MS spectrometer (Agilent, USA). A VF-5MS (Varian, USA), 30 m×0.25 mm I.D., and a fused-silica capillary column of 0.25 μm film thickness was used. The carrier gas was high purity helium (99.999%, 1.0 $mL·min^{-1}$). The temperature program was used as follows: 80 ℃ held for 3 min, ramp to 150 ℃ at a heating rate of 15 $℃·min^{-1}$, then ramp to 200 ℃ at 5 $℃·min^{-1}$, and finally ramp to 300 ℃ at 10 $℃·min^{-1}$, held for 8 min. The injector temperature was set at 250 ℃, and 1 μL analyte was injected in the splitless mode. The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The temperature at MS ion source was 230 ℃. The qualitative analysis was processed through the scan mode. Scan range was 40−350 amu. The quantitative analysis was processed through the selective ion mode (SIM) using the internal calibration method. Chrysene-d12 was employed as an internal standard. The selected characteristic ions of benz[a]anthracene were 228, 226, and 229.

2   Results and discussion

2.1   *In situ* analysis using DRIFTS

The diffuse reflectance spectra of the photochemical reaction of benz[a]anthracene on the TiO$_2$ surface, under direct irradiation, are shown in Fig.1. Before irradiation, the spectrum showed several characteristic benz[a]anthracene absorption peaks at 3050, 3030, 3003, 1948, 1924, 1500, 1476, 1413, and 1338 cm^{-1}, which were in agreement with the literature[10,11]. The peaks appeared at 3050, 3030, and 3003 cm^{-1} for aromatic C−H stretching vibrations, 1948 and 1924 cm^{-1} for benz[a]anthracene aromatic overtone C−H bending vibrations, 1500 and 1476 cm^{-1} for benz[a]anthracene aromatic C−C ring stretching vibrations[12], and 1413 and 1338 cm^{-1} for benz[a]anthracene aromatic C−H bending vibrations.

The characteristic absorption peaks of benz[a]anthracene were removed, for the most part, after irradiation, indicating that benz[a]anthracene was photodegraded on the TiO$_2$ surface by the ring-opening reaction or C−H of the benzene ring replaced reaction. The spectra after irradiation showed two new sharp peaks at 1667 and 1590 cm^{-1}, and the area of both peaks increased during the irradiation process. These peaks corresponded to the C=O stretching vibrations and C=C stretching vibrations, respectively. These findings clearly indicated that the products mainly contained C=O and C=C functional groups. The identification of photochemical products on the TiO$_2$ particles was carried out by GC-MS after SFE extraction. The GC-MS results of the products are presented in Fig.2. Peak I in the gas chromatogram was benz[a]anthracene. Peak II was the reaction product (Fig.2a) and was analyzed in detail by mass spectroscopy (Fig.2b). The mass spectrum matched that of the NIST library spectrum of benz[a]anthracene-7,12-dione with a 98% fit. The base peak (Fig.2b) at *m/z*=258 corresponded to the molecular weight of benz[a]anthracene-7,12-dione[13], so the reaction product was most likely benz[a]anthracene-7,12-dione.

The bands at 3697 and 3726 cm^{-1} corresponded to the isolated hydroxyl groups on the TiO$_2$ surface[14]. During irradia-
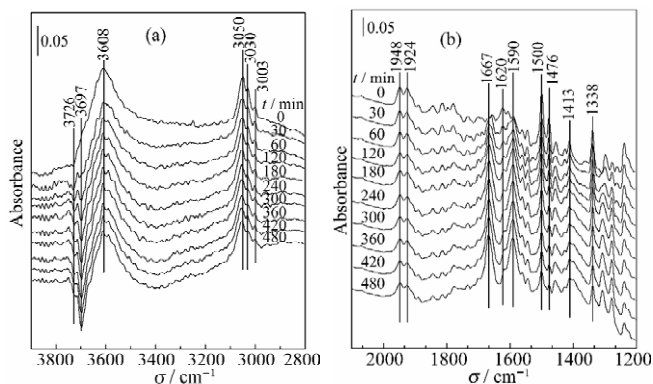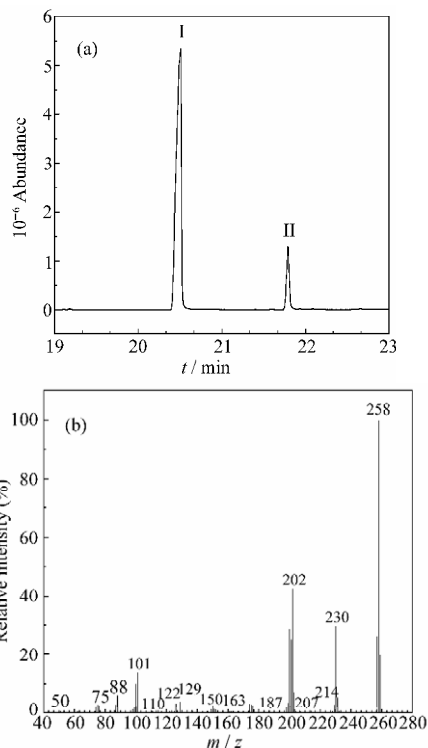

Fig.2   (a) Gas chromatogram of the intermediate products of B[a]A/TiO$_2$ after 480 min of photochemical reaction; (b) mass spectrum of the major GC component II

tion, the bands at 3697 and 3726 cm^{-1} appeared as negative peaks, and gradually increased, indicating that the surface hydroxyl attended the reactions. It was also observed that a broad band centered at 3608 cm^{-1} and a band at 1620 cm^{-1} were gradually decreased during irradiation. These bands were assigned to H$_2$O adsorbed on the TiO$_2$ surface. It was probably TiO$_2$ surface absorbed water dissociated to form surface hydroxyl[15], and continually supplying OH for the reaction.

2.2   Photochemical reaction kinetics

It allows one to scale the kinetics of the product′s functional groups in the photooxidation process according to the integrated area of the corresponding IR absorbance bands as a function of irradiation time[16]. The evolution of the relative integrated area of selected bands as a function of irradiation time is shown in Fig.3. Fig.3(a−c) shows the results of the OH, C−H, and C−C groups, and Fig.3(d, e) shows the results of the C=O and C=C groups. During the initial period of irradiation, the surface hydroxyl decreased fast, and the rate appreciably declined after prolonged irradiation. It shows a similar tendency with the C−H, C−C, C=O, and C=C groups in benz[a]anthracene, indicating that photochemical progress is most probably related to surface hydroxyl.

The integrated area of C−H and C−C bands were 69% and 33%, respectively, for the original, after 480 min irradiation, indicating that only a small amount of benz[a]anthracene was photodegraded. It was because of the smaller penetration
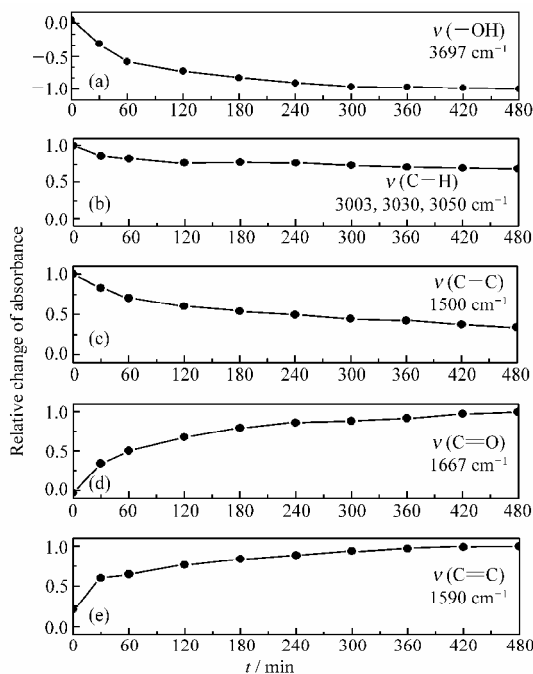

Fig.1   *In situ* DRIFTS spectra of the benz[a]anthracene (B[a]A)/TiO$_2$ sample during the photochemical reaction at 25 ℃
(a) 2800−3900 cm^{-1}; (b) 1200−2100 cm^{-1}

Fig.3 Kinetic behaviors for consumption of hydroxyl and benz[a]anthracene during the photochemical reaction and for production of oxidized products

Fig.4 Changes in the benz[a]anthracene concentration during the photochemical reaction

depth of the Xe lamp light as compared to the infrared radiation. The Xe lamp light could not irradiate the bottom layer samples in the sample cell, so the photochemical reaction did not occur on the bottom TiO_2 particles. Otherwise the infrared radiation can get information of deeper samples for its larger penetration depth. On the other hand, it was possible that the reaction sites of benz[a]anthracene were at the middle benzene ring, thus, there are different effects on C−H and C−C groups.

To further study the photodegradation rate of benz[a]anthracene adsorbed on TiO_2, an additional experiment was carried out as follows: B[a]A/TiO_2 placed in the quartz cells was irradiated by an Xe lamp directly (22 mW·cm^{-2}). At given reaction time intervals, certain amount of samples were got, and subsequently extracted by SFX and further quantitatively analyzed by GC-MS. The concentration of benz[a]anthracene in the unirradiated sample was 1.68 mg·g^{-1} and it was 0.09 mg·g^{-1} after 120 min irradiation (Fig.4). The process of benz[a]anthracene photodegradation on the TiO_2 particles matched the exponential decay equation, and the half-life time was 6.8 min. The radiant flux of the sun was 20 mW·cm^{-2} at 14:00 pm, 1.5 m above ground, measured by a photometer. The radiant flux of the Xe lamp used in the experiments was relatively closer to sunlight, thus, the research results could be used for characterization of the photochemical reaction of benz[a]anthracene on TiO_2 particles, under atmospheric conditions, to a certain degree. As Behymer et al.[4] have reported, half-life time for the photolysis of benz[a]anthracene, adsorbed on silica gel, alumina, and coal fly ash were 240 min, 120 min, and 38 h, respectively. To understand the effect of direct photolysis on benz[a]anthracene photodegradation, the
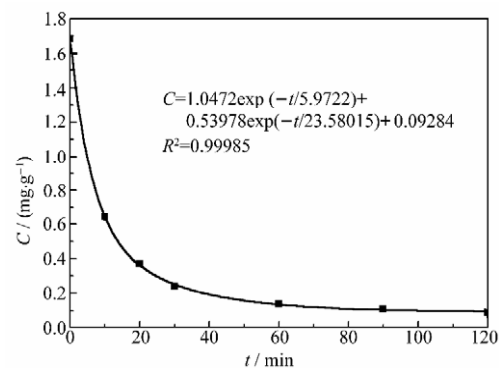
photochemical experiment of benz[a]anthracene adsorbed on nano-silica particles was carried out. The results showed that benz[a]anthracene concentration was 1.23 mg·g^{-1} before reaction and 1.19 mg·g^{-1} after 120 min irradiation. The reaction rate was far below from where the reaction occurred on the TiO_2 surface, indicating that the TiO_2 contained in the atmospheric particles contributes more and greatly to the photochemical reaction of benz[a]anthracene on the troposphere aerosol particles and its role should not be neglected.

2.3 The influence of irradiation wavelength on the photochemical reaction

To study the influence of light wavelength on the photochemical reaction, the reaction process, irradiated with wavelength light greater than 450 and 350 nm, was compared with the whole band, by using two cutoff filters to remove certain wavelengths of light. The results showed that irradiated with the light of wavelength greater than 450 nm, the entire infrared spectra had no significant change, and the change in the infrared spectra irradiated with the wavelength greater than 350 nm was similar to the whole band case, with negative peaks appearing at 3697 and 3726 cm^{-1}, and new sharp peaks appearing at 1667 and 1590 cm^{-1}. At the same time the characteristic absorption peaks of benz[a]anthracene at 3050, 3030, 3003, 1948, 1924, 1500, 1476, 1413, and 1338 cm^{-1} greatly decreased. Fig.5 shows the *in situ* DRIFTS of the B[a]A/TiO_2 sample after 480 min irradiation under different wavelength lights in the range of 1200−1900 cm^{-1}. There were no significant product peaks in the infrared spectra of B[a]A/TiO_2 irradiated with the light of wavelength greater than 450 nm, because the band gap of TiO_2 was 3.2 eV, its UV-visible absorption edge was 387 nm, and the photocatalytic reaction could not occur on the TiO_2 surface irradiated with the light of wavelength greater than 450 nm. Irradiated with the lights of wavelength bigger than 350 nm, the infrared spectra of B[a]A/TiO_2 were similar to those irradiated with the whole band lights, but the integrated area of product bands were smaller for lower radiation energy and intensity. The solar irradiation reaching the troposphere is with the wavelength
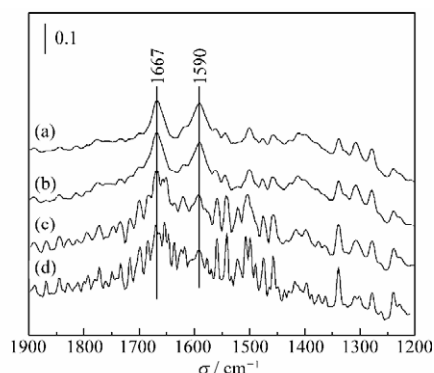
Fig.5 *In situ* DRIFTS of the B[a]A/TiO₂ sample after 480 min
irradiation under different wavelength lights
(a) full wavelength; (b) λ>350 nm; (c) λ>450 nm; (d) black

bigger than 300 nm, which is enough to induce the TiO₂ particles by producing photo-excited electrons and holes, and subsequently participating in the atmospheric photochemical reaction. Therefore, the photocatalytic oxidation of benz[a]anthracene on the surface of TiO₂ particles in the tropospheric atmosphere is possible, and can accelerate the photodegradation of benz[a]anthracene.

2.4 Reaction mechanism

Bonamali *et al*. studied the photocatalytic degradation of naphthalene and anthracene over thin films of TiO₂ particles[17], and the photoproducts were 5,8-dihydroxynaphthaquinone and 9,10-anthraquinone. Calculated by frontier electron density, the most reactive sites of benz[a]anthracene are at the 7 and 12 positions, and the oxidation product is benz[a]anthracene-7,12-dione[18]. In this experiment, the remarkable changes in the infrared spectra were the appearance of two new sharp peaks at 1667 and 1590 cm⁻¹, corresponding to the C=O stretching vibrations and C=C stretching vibrations, respectively. The C−C bond in the benzene ring is a delocalization of the π bond, which is a special bond between C−C single bond and C=C double bond. The formation of C=O bond brought the C−C bond in the benzene ring of benz[a]anthracene much closer to the C=C, thus a sharp peak generated at 1590 cm⁻¹. Thus, the peaks of 1667 and 1590 cm⁻¹ are the characteristic absorption peaks of benz[a]anthracene-7,12-dione according to the standard infrared spectra. By combined additional GC-MS analysis, it was confirmed that the main product of the heterogeneous photochemical of benz[a]anthracene on the surface of TiO₂ particles was benz[a]anthracene-7,12-dione. Kohtani *et al*.[19] investigated the photooxidation degradations of benz[a]anthracene using pure and Ag-loaded BiVO₄ photocatalysts in acetonitrile under visible light irradiation, and the main photoproduct was benz[a]anthracene-7,12-dione. Jang *et al*.[13] reported that the product of benz[a]anthracene photodegradation was benz[a]anthracene-7,12-dione, after direct irradiation of benz[a]anthracene. These previous studies sug-

gested that both the photoproducts of benz[a]anthracene contained benz[a]anthracene-7,12-dione by photolysis or photocatalytic oxidation. To understand the role of oxygen, the photochemical experiment was carried out in air, oxygen, and argon atmosphere, respectively. The experimental observations indicated that a high concentration oxygen greatly enhanced the photochemical reaction rate, suggesting that O₂ was involved in the reactions, which was in agreement with the photocatalytic reaction mechanism[20]. Combined with the changes of surface hydroxyl and surface oxygen in the reaction process, it was considered that surface hydroxyl and surface oxygen played key roles in the reaction, and that the surface absorbed water dissociated to form the surface hydroxyl supplying ˙OH for the reaction. Based on these results, the possible photochemical mechanism of benz[a]anthracene was proposed in Fig.6. First, the benz[a]anthracene was attacked by ˙OH radicals to form adducts, which further reacted with O₂ by removing H₂O, after which benz[a]anthracene-7,12-dione was obtained.
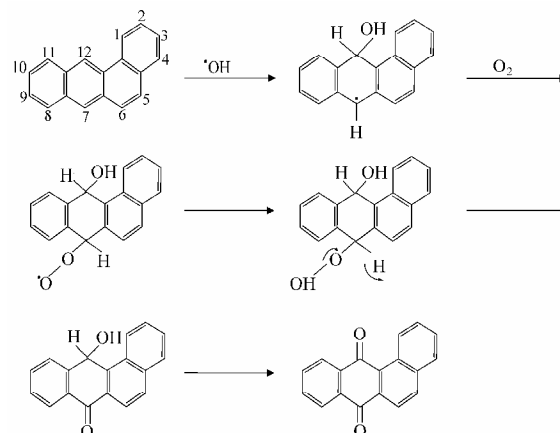

Fig.6 Proposed reaction mechanism for the photooxidation of
benz[a]anthracene on TiO₂ particles

3 Conclusions

Irradiated with Xe lights, the photocatalytic oxidation of benz[a]anthracene occurred on the surface of TiO₂ particles, and the main photoproduct was benz[a]anthracene-7,12-dione. Surface hydroxyl and surface oxygen played key roles in the reaction.

Under simulated sunlight irradiation (22 mW·cm⁻²), the process of benz[a]anthracene photodegradation on TiO₂ particles matched the exponential decay equation, and the half-life time was 6.8 min. The TiO₂ content in tropospheric aerosol particles is relatively low compared to SiO₂ and Al₂O₃, but the photodegradation rate of benz[a]anthracene on the surface of TiO₂ particles is enhanced significantly, therefore, the role of TiO₂ on benz[a]anthracene photodegradation must not be neglected.

References

1 Wang, L. S. Chemistry of organic pollutants. Beijing: Higher Education Press, 2004: 591

2 Fioressi, S.; Arce, R. *Environ. Sci. Technol*., **2005, 39**: 3646

3 Reyes, C. A.; Medina, M.; Crespo-Hernandez, C.; Cedeno, M. Z.; Arce, R.; Rosario, O.; Steffenson, D. M.; Ivanov, I. N.; Sigman, M. E.; Dabestani, R. *Environ. Sci. Technol*., **2000, 34**: 415

4 Behymer, T. D.; Hltes, R. A. *Environ. Sci. Technol*., **1985, 19**: 1004

5 Huang, G. L.; Zhuang, Y. Y.; Dai, S. G. *Acta Scientiarum Naturallum Universitatis Nakaiensis*, **1997, 30**(1): 98

6 Wang, W. X.; Su, Y. H.; Li, J. H. *China Environmental Science*, **1997, 17**(2): 97

7 Jang, M.; McDow, S. R. *Environ. Sci. Technol*., **1995, 29**(10): 2654

8 Zakharenko, V. *Topics Catal*., **2005, 35**(3−4): 231

9 Vogt, R.; Elliott, C. H.; Allen, C.; Laux, J. M.; Hemminger, J. C.; Finlayson-Pitts, B. J. *Atmospheric Environment*, **1996, 30**(10−11): 1729

10 Naziruddin, K. M.; Al-DWayyan, A. S.; Zaidi, Z. H. *Chin. Phys. Lett*., **2006, 23**(9): 2407

11 Hudgins, D. M.; Sandford, S. A. *J. Phys. Chem. A*, **1998, 102**: 329

12 Jing, X. Y.; Chen, S. D.; Yao, E. Y. Introduction to infrared spectroscopy. Tianjin: Scientific & Techincal Press, 1992: 158

13 Jang, M.; McDow, S. R. *Environ. Sci. Technol*., **1997, 31**(4): 1046

14 Bezrodna, T.; Puchkovska, G.; Shymanovska, V.; Baran, J.; Ratajczak, H. *J. Mol. Struct*., **2004, 700**: 175

15 Henderson, M. A. *Surf. Sci. Rep*., **2002, 46**: 1

16 Panayotov, D. V.; Paul, D. K.; Yates, J. T. *J. Phys. Chem. B*, **2003, 107**: 10571

17 Bonamali, P.; Maheshwar, S. *J. Mol. Catal*., **2000, 160**: 453

18 Lee, B. D.; Hosomi, M.; Masaaki, H. *Chemosphere*, **2001, 42**: 431

19 Kohtani, S.; Tomohiro, M.; Tokumura, K.; Nakagaki, R. *Appl. Catal. B*, **2005, 58**: 265

20 Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemannt, D. W. *Chem. Rev*., **1995, 95**: 69