



NO_x removal from vehicle emissions by functionality surface of asphalt road

Meng Chen^a, Yanhua Liu^{b,*}

^a College of Traffic, Northeast Forestry University, 26 Hexing Road, Harbin 150040, People's Republic of China

^b College of Wildlife Resources, Northeast Forestry University, 26 Hexing Road, Harbin 150040, People's Republic of China

ARTICLE INFO

Article history:

Received 27 June 2009

Received in revised form

11 September 2009

Accepted 11 September 2009

Available online 23 September 2009

Keywords:

Photocatalysis

Road surface materials

Titanium dioxide

NO_x decomposition

ABSTRACT

This paper reported the potential of heterogeneous photocatalysis as an advanced oxidation technology for NO_x removal from vehicle emissions by using TiO₂ as a photocatalyst immobilized on the surface of asphalt road. Based on asphalt road material porous characteristic, we utilized permeability technology to make asphalt nano-TiO₂ to be environmental protection materials. And then using scanning electron microscope, we observed the penetrating effect of TiO₂. The effect of surface friction, humidity and light intensity on NO_x removal had been systematically investigated by the use of TiO₂ immobilized on the surface of asphalt road as photocatalytic environmental protection materials. In addition, the decontaminating effect was tested by contrast test in TiO₂ spraying section with non-spraying section, while the productions were used in road environment. Results of experiment revealed that decontaminating rate of the productions ranged from 6% to 12% this kind of photochemical catalysis environmental protection material has good environment purification function.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The NO_x (NO + NO₂) from automobile emission was a main of atmosphere pollution material, which had been huge harm to human health. So, many countries had conducted massive research in the automobile manufacture aspect in order to reduce automobile exhaust. With the rapid increase of automobile inventory, high NO_x concentrations were often observed in highways because the total emissions quantity increased steadily. Consequently, reducing NO_x level in the environment (especially round highway) was strongly appealed by people.

The use of TiO₂ photocatalyst in combination with construction materials had shown a favorable synergetic effect in the removal of air pollutants [1]. In view of the fact that automobile emission contacted with the road surface in the first time, it was one feasible method that photocatalyst is immobilized in the road surface to purify automobile pollutants. In recent years, a wide number of laboratory scale tests had been performed, under the different experimental conditions, in order to evaluate the de-polluting properties of TiO₂ photocatalytic materials [2–5]. Cassar reported that NO_x removal from air due to adsorption and photocatalysis on TiO₂ containing (5% by weight) cement [6]. On lab-scale, NO_x removal efficiency up to 92% was obtained after exposure to a 300 W lamp for 7 h. TiO₂ and cement were combined to use towards

NO_x removal that showed a synergetic effect. Accordingly, some local governments that suffer from NO_x pollution have started evaluating the performance of photocatalytic air-purifying materials on larger scales. A full-scale experiment had been performed in Segrate (Italy) where photocatalytic mortar was applied to 6000 m² of an urban road with vehicle traffic of 1200 units per hour. On a sunny summer day (illumination > 90,000 lx, wind speed < 0.7 m s⁻¹), a 50% reduction in NO_x was measured, with a stability for at least 1 year of application [6]. The field tests showed that TiO₂ may effectively purify NO_x from vehicle emission for a long time, which could be used for applications in roadway structures. However, many highways surface materials were the bituminous, if the nanometer photochemical catalysis technology could be applied in the bituminous pavement; it had the great significance to purify automobile pollutants on the roadway. Hence, the research focused on the nanometer TiO₂ immobilized method and degeneration effect on asphalt road.

2. Experimental

2.1. Materials

Nanometer TiO₂ (anatase, its diameter was 10–30 nm and surface area of 50 m² g⁻¹) was provided by the Laboratory of Center for Composite of Harbin Institute of Technology. Penetrant was obtained from College of Traffic, North-east Forestry University. Silane coupling reagent KH-570, was purchased from Nanjing Shuguang Chemical Group Co., Ltd. All other chemicals were of analytical grade. Doubly distilled deionize water was used throughout the experiment.

* Corresponding author.

E-mail addresses: chenmeng623@126.com (M. Chen), liuyanhua815@126.com (Y. Liu).

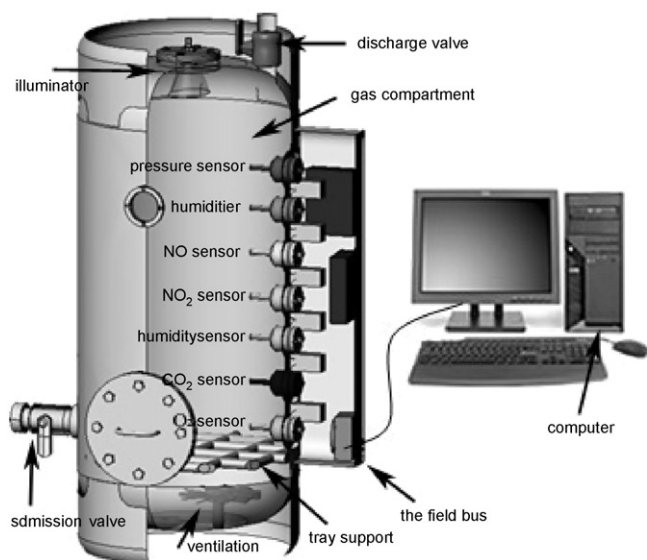


Fig. 1. Decontamination test reactor of vehicle emissions.

Surface modification was carried out through vigorous stirring the appropriate amount of nanoparticles TiO_2 for 30 min in the saturated solution of silane coupling reagent at 60°C . Filtered with $0.45\ \mu\text{m}$ membrane filter, the modified TiO_2 was washed with water three times, heat-treated for 30 min at 105°C . Then a white powder was obtained, which was the surface-modified nanoparticles of TiO_2 with silane coupling reagent.

Based on “Technical specifications for construction of highway asphalt pavements”, we selected AC-16 to carry on asphalt specimen preparation that was constituted of MAC-70# asphalt, the crushed stone, the sand and the powdered ore. At last, according to surface of asphalt road porous characteristic, we carried on penetrating load.

2.2. Photocatalytic degradation experiments: reactor and set-up

According to American Material Test Association standard (ASTM D 5116-1990) and Japan industrial standard (photochemical catalysis material–air purification performance test method), we designed the simulation purification examination reactor. Stainless steel was used to make the reactor for requirement of low adsorption ability and resistance to ultraviolet irradiation. This reactor was set-up by gas compartment, illuminator, ventilator, tray support, admission valve, discharge valve, humidifier, sensor (pressure, humidity, temperature and NO_2 , NO), field bus, switch (RS-232/RS-485 signal shifter) and computer. The picture of reactor was described in Fig. 1. When this test reactor worked, the photochemical catalysis environmental protection material was measured by being putted in the gas compartment on the tray support. Then, exhaust was discharged from automobile at some kind of operating mode, entered the gas compartment through admission valve control. When the gas compartment was balanced, the test would begin. The harmful ingredient density change of automobile exhaust should be dynamically monitored through various sensors and saved by the computer auxiliary test system with the Kingdom software compilation.

Three tests were performed by the use of above-described reactor:

(1) Purification experiment:

In order to test purifying effect of photochemical catalysis material we had carried on bituminous photochemical catalysis

environmental protection material purification performance test. At the same time, because the road surfaces were worn frequently in the actual driving process, we polished the test specimen to some extent to test purifying effect.

(2) Environmental factor effect experiment:

Humidity influence: H_2O molecule adsorbed on surface of TiO_2 was the essential materials to produce main oxide compound of photochemical catalysis response. This research carried on experiment about humidity influence on purification through changing humidity environment's priority order.

Test 1: Firstly, humidity of reactor interior was controlled. And then, the exhaust of automobile was passed over the reactor, when it achieved corresponding humidity.

Test 2: Firstly, the exhaust of automobile passed over the reactor. And then, when the exhaust achieved balance, humidity of reactor interior was controlled for purifying.

Illumination influence: TiO_2 photocatalyst removing harmful gas effectively depended on ultraviolet ray illumination. The ultraviolet ray illumination can caused electron–hole pairs to form on the photocatalyst surface and the electron–hole pairs purified NO_x . So we may find that the ultraviolet illumination was the essential condition of photochemical catalysis response. Light intensity and wavelength of light were controlled to influence the photocatalytic decomposition of NO_x .

(3) The practical application test:

In order to examine practical applying effect in the traffic environment outside, the TiO_2 photochemical catalysis material was applied to purify vehicle emission pollutant on the road. The road was the section of federal highway G11 from Tsitsihar to the Nehe River.

2.3. Analytical methods

2.3.1. Scanning electron microscopy

The SEM used was a commercial Hitachi S2300 instrument with a tungsten hairpin filament. An accelerating voltage of 25 keV was used and samples were on gold to eliminate charging.

2.3.2. Transmission electron microscopy

Transmission electron microscopy analyses were performed by using a JEM-2010 (JEOL) operating at 160 kV. The penetrating solution dispersing surface-modified TiO_2 nanoparticles were dried slowly on an amorphous carbon supported on a copper mesh grid. The research dispersed and sizes of nanoparticles were determined and observed by the TEM images.

2.3.3. Test facility

We used the reactor (Fig. 1) to carry on the automobile exhaust practical application examination on the purification effect of photochemical catalysis.

3. Results and discussion

3.1. Physical properties

In Fig. 2, we may discover that, nanometer TiO_2 was well dispersed in penetrant. These results confirmed that the phenomena of nanoparticles agglomeration decreased effectively for preparing nanometer TiO_2 solution through synthesis dispersed method. Firstly, ultrasonic wave dispersed nanoparticles to tiny pellet. Secondly, high speed rotary caused solution mixed in wide range. In addition, suitable surface modification made pellet surface adsorb certain high polymer and created steric hindrance, which hindered pellet further to grow-up effectively. So the measure improved the nanometer granule dispersed.

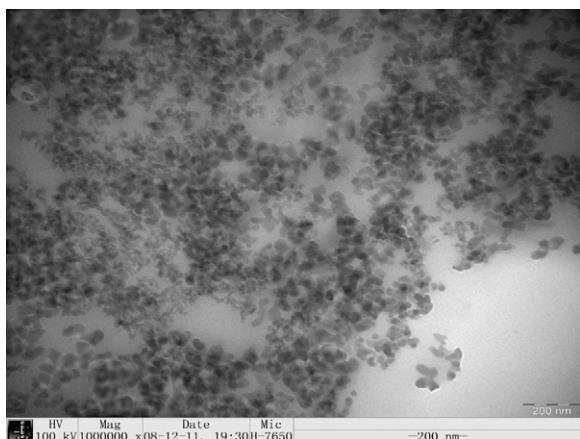


Fig. 2. TEM image of penetrating solution.

TiO₂ solution coatings were conventionally prepared by atmospheric plasma spraying technique using a Plasma-Technik 2000 console and a F4 torch (Sulzer-Metco). The solution feed rate, ensured a stable feeding rate of feedstock material in plasma, was fixed at 14 g min⁻¹. In liquid spraying process, the initial suspensions droplets were fragmented into smaller ones. Secondly, the solvent was evaporated from the droplets. It can clearly be seen (Fig. 3). The nanometer TiO₂ solution was well penetrated load on the road surface hole and had not presented obvious agglomeration phenomenon. At the same time, dense tiny honeycomb-shaped hole and the gully in the surface of road increased adsorption probability of pollutant in the superficial. Such enhanced the nanometer TiO₂ photochemical catalysis activeness and degeneration rate.

3.2. Photocatalytic properties

In order to test decontaminating effect of photochemical catalysis material, we used effective decontaminating rate (1), the photocatalytic rate (2) and the photocatalytic activity (3) to evaluate a kind of testing system designed by us. The experiments were divided into two stages. The first stage of the test was standard specimen decontaminating effect. Firstly, road surface material adsorption function was tested under closed ultraviolet source. Next, the ultraviolet source was opened in order to carry out the decontaminating function test on nanometer photochemical catalysis material. The second stage was to test decontaminating effect of wore standard specimen. Because the road surface worn frequently in the actual driving process, the test specimen polished

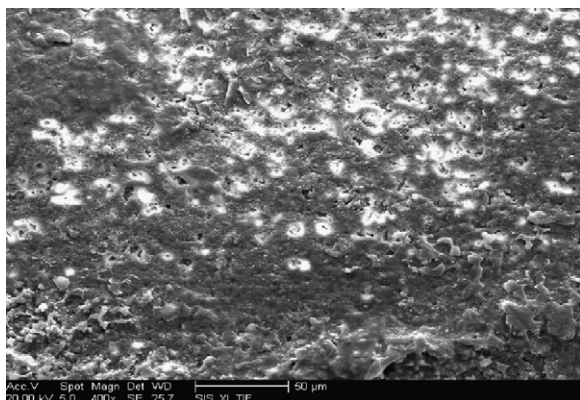


Fig. 3. SEM image of road surface after penetrated load.

Table 1
Degradation effect of parameter on NO_x.

Photochemical catalysis material	NO			NO ₂		
	η	PR	PA	η	PR	PA
Asphalt-based	23.60	0.06	0.009	29.94	0.09	0.008
Asphalt-based after wear	20.80	0.04	0.007	24.60	0.07	0.007

to some extent to was tested by decontaminating effect:

$$\eta = \left(\frac{C_{in} - C_{suv}}{C_{in}} - \frac{C_{bin} - C_{sb}}{C_{bin}} \right) \times 100\% \quad (1)$$

where η is effective purifying rate, %; C_{in} represents the initial steady-state pollutant concentration (before turn on the UV source), mg m⁻³; C_{suv} represents the pollutant concentration during irradiation phase, mg m⁻³; C_{bin} represents the initial steady-state pollutant concentration, mg m⁻³; C_{sb} represents the pollutant concentration at the end of the blank experiment (without irradiation):

$$PR = \frac{C_r}{S} \times Q \quad (2)$$

where PR is the photocatalytic rate, mg m⁻² s⁻¹; C_r represents the pollutant concentration removed by the TiO₂ effect, mg m⁻³; S represents the sample area exposed to the irradiation; the airflow of ventilator:

$$PA = \frac{PR}{(C_{in} + C_{suv})/2} \quad (3)$$

where PA is the photocatalytic activity, cm s⁻¹; C_{suv} represents the pollutant concentration during irradiation phase, mg m⁻³.

In Table 1, we can find that two kinds of the photochemical catalysis materials had good decontaminating effect to NO_x discharge by vehicles. In purifying NO and the NO₂, the photocatalytic rate of the two kinds of photochemical catalysis material was higher than 20% and had the same value about 0.01 cm s⁻¹ in the photocatalytic activity. This was mainly reason that the bituminous pavement had small size scored surface and TiO₂ penetrating solutions have good wet ability making non-material very easy to penetrate pore and the slit of bituminous pavement scored surface. The penetrating solutions had formed effective thin film after its solidification. Another factor was that actual contacted area was nanometer TiO₂. And the scored surfaces were bigger than its geometry area. If the contacted area was bigger, the adhesion was bigger under the unit contacted. It guaranteed attrition material limited loss and the photochemical catalysis function.

3.3. Humidity effect

In Fig. 4, under the homogeneous humidity was latter changed, TiO₂ increased purification effect to the NO_x when ambient humidity increased gradually. It usually was explained that TiO₂ photocatalyst had great surface area easily adsorbed moisture of environment. Under ultraviolet ray illumination, the moisture content can provide photoproduction hole hydroxyl producing the oxidized very high hydroxyl free radical. The hydroxyl free radical promoted photochemical catalysis to oxidize NO_x. Therefore high-moisture environment purification effect turned much better than low humidity environment. However, excessive water vapor on the catalyst surface will inhibit the reaction because the presence of water vapor competed with pollutants for adsorption sites on the photocatalyst.

When the homogeneous humidity was firstly changed, the purification effect turned worse. It indicated the humidity priority controlled had significant effect to NO_x decontamination. Based on a competition mechanistic approach, the increase in humidity

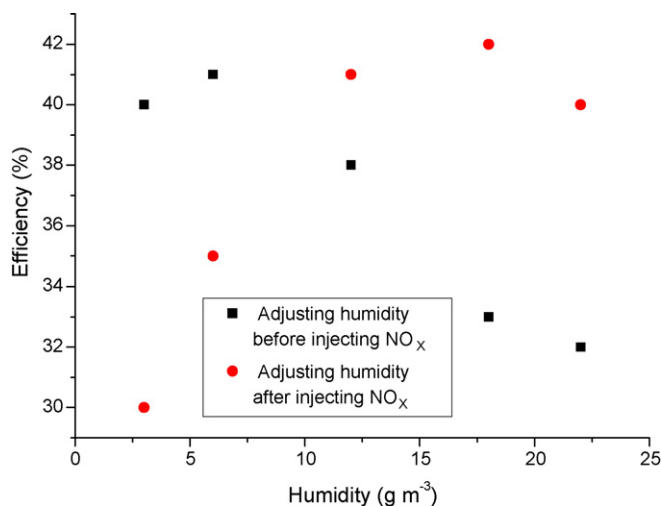


Fig. 4. Decontamination efficient of NO_x under different humidity.

would act to remove some of the NO_x from the catalyst surface [7]. Thus, once humidity was same, the purification effect was also same. However, the data from this study showed that purification effect was different. Hence, the research carried on a certain supposition elaboration to it.

The prerequisite for photocatalytic decomposition of NO_x is that the NO_x molecule must reach the photocatalyst interface or at least contact a radical species on the solid/gas interface. However, the water molecules possibly forming the boundary layer to preclude NO_x molecules could approach photocatalyst interface or radical species.

It has been reported that at concentrations of 1% water vapor in air (at 380 K which is equivalent to 5776.6 mg m⁻³, thus 25.0% RH at 25 °C), the coverage of water molecules on the TiO₂ (specific surface area ≈ 250 m² g⁻¹) is between 0.3 and 3 ML, where 1 ML is defined as a bilayer of water molecules (1.15 × 10¹⁵ molecules cm⁻²) [8]. Since adsorption affinity reduces with increasing temperature [9], it is reasonable to postulate that at room temperature (293 K), the water coverage is larger than 0.3–3 ML. Furthermore, the TiO₂ of surface area is 50 m² g⁻¹. This is much less than 250 m² g⁻¹, further enhancing the number of layers formed by water molecule.

So we may explain to Fig. 4, at dry conditions, environment contained little moisture, water molecule was difficult to form thick thin film on the TiO₂ surface. Thus, NO_x molecules can compete to adsorb on the surface of photocatalyst, or dissolve into H₂O molecules, which may have already adsorbed onto the photocatalyst receptor sites. Purification effect was not significant influence through change humidity change. At high humidity, because the moisture content was the same, NO_x adsorbed by the water molecule was also basically same. If humidity environment was firstly changed, the moisture content will be adsorbed ahead of time on the TiO₂ surface and form thin film. The competition for adsorption sites was overwhelmed by greater proportion of water molecules. The resultant film of water precluded NO_x from adsorbing on the catalyst, from adsorbing to water molecules adjacent to the photocatalyst interface. At last, it caused purification effect decreased.

3.4. Light source effect

The functional dependence of the photocatalytic reaction rate on UV intensity is shown in Fig. 5. Under the UV intensity from 0 to 1 mW cm⁻² illumination, the photocatalytic reaction rate increased linearly with the light intensity. It proved the electron–hole pairs were consumed more rapidly by the chemical reactions in the process. On the other hand, from 2 to 4 mW cm⁻² UV illumination,

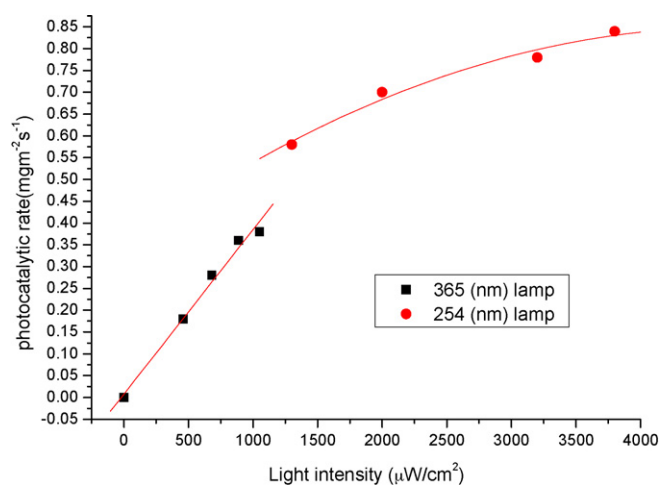


Fig. 5. Photocatalytic rate of NO_x under different UV source.

the reaction rate increased with the square root of light intensity. It showed the recombination of holes and electrons had been a dominant process. These were similar to the results obtained by Okamoto et al. [10].

Another factor to impact on the photocatalytic decomposition of NO_x is wavelength of the UV light. It may be analyzed by band gap energy and adsorbed ability. Band gap energy (E) was the energy needed for photocatalytic activity. The relationship between band gap energy of TiO₂ and wavelength of light was:

$$E = hv = \frac{hc}{\lambda} \quad (4)$$

where h is Planck's constant, ν is the frequency of light, c is the velocity of light, and λ is the wavelength of light [11].

From formula (4) calculated, we may find that 254 nm irradiation would engender higher band gap energy. It resulted electron and hole oxidation ability stronger. At the same time, the literature [12] had reported that shorter wavelength light is adsorbed more strongly by TiO₂ than the longer one. Therefore, the penetration distance of photons into TiO₂ is shorter. The electrons and holes are formed closer to the surface of the particles. Then, they take less time to migrate onto the surface of the particle and, hence, have less time to participate in the energy wasting recombination reactions before useful surface reaction takes place. The shorter wavelength of 254 nm irradiation is more effective in promoting the photocatalytic decomposition of NO_x than the longer wavelength of 365 nm irradiation.

3.5. The practical application

The experiment applies contrast test. We arrange three air samplers to carry on the synchronized sampling in immobilization and non-immobilization range, respectively, as well as use the multi-purpose weather stations to gather dynamic data in external environment condition. Finally, we use the UV–vis spectroscopy (TU-1901) to carry on determination absorbency of gathered sample by N-(1-naphthyl)-cetylncndiaminc dihydrochloride colorimetric. The entire test work was executed under nature flow condition in the daytime and each specimen test last 1 h. The entire test work had already been carried on 3 months on the spot.

It has remarkable difference between the NO_x density of the experimental road immobilized nanomaterials and not immobilized nanomaterials in the asphalt road (Table 2). Meanwhile, the biggest NO_x decontaminating rate may achieve more than 10% and the lowest NO_x decontaminating rate may also achieve 6.56% in the contrast experiment. The test result is obtained in the natural condition affected by wind, temperature and humidity. So, it

Table 2
Degradation effect of different on NO_x.

Test spot	Difference		Decontaminating rate (%)	
	<i>F</i>	<i>p</i>	Max	Min
TiO ₂ load 1–non-TiO ₂ load 1	8.1596	0.0064	12.1	6.56
TiO ₂ load 2–non-TiO ₂ load 2	8.3736	0.0058	9.56	6.07
TiO ₂ load 3–non-TiO ₂ load 3	6.5661	0.0137	10.05	7.28

is feasible that nano-TiO₂ can purify vehicle emission pollutant in actual traffic environment.

4. Conclusions

According to the characteristic of asphalt road material, we utilized permeability technology to make environmental protection materials of asphalt nano-TiO₂. We have carried out the indoor simulation of road traffic environment through simulating purification examination system design by us. The experiment indicated that the kind of photochemical catalysis environmental protection material has good environment purification function. In addition, purifying rate of vehicle pollutant of the road surface nanometer photochemical catalysis material ranged from 6% to 12% under actual outdoor road traffic environment. Hence, nano-TiO₂ can purify vehicle emission pollutant in actual traffic environment.

Acknowledgement

This work was supported by funding (contract no. 200631800083) from the Western Region Communications Construction Project of China.

References

- [1] A. Fujishima, K. Hashimoto, T. Watanabe, TiO₂ Photocatalysis: Fundamentals and Applications, BKC, Inc., Japan, 1999.
- [2] C.H. Ao, S.C. Lee, C.L. Mak, L.Y. Chan, Photooxidation of VOCs and NO for indoor purification using TiO₂: promotion versus inhibition effect of NO, Appl. Catal. B: Environ. 42 (2003) 119–129.
- [3] S. Devahasdin, C. Fan, K. Li, D. Chen, TiO₂ photocatalytic oxidation of nitric oxide: transient behavior and reaction kinetics, J. Photochem. Photobiol. A: Chem. 156 (2003) 161–170.
- [4] J.S. Dalton, P.A. Janes, N.G. Jones, J.A. Nicholson, K.R. Hallam, G.C. Allen, Photocatalytic oxidation of NO_x gases using TiO₂: a surface spectroscopic approach, Environ. Pollut. 120 (2002) 415–422.
- [5] K. Hashimoto, K. Wasada, M. Osaki, E. Shono, K. Adachi, N. Toukai, H. Kominami, Y. Kera, Photocatalytic oxidation of nitrogen oxide over titania–zeolite composite catalyst to remove nitrogen oxides in the atmosphere, Appl. Catal. B: Environ. 30 (2001) 429–436.
- [6] L. Cassar, Photocatalysis of cementitious materials: clean buildings and clean air, MRS Bull. 29 (2004) 328–331.
- [7] L.A. Dibble, Fluidized-bed oxidation of trichloroethylene in contaminated airstream, Sci. Technol. 26 (1992) 492–495.
- [8] C. Ha'gglund, B. Kasemo, L. Osterlund, In situ reactivity and FTIR study of the wet and dry photooxidation of propane on anatase TiO₂, J. Phys. Chem. 109 (2005) 10886–10895.
- [9] J.F. Wu, C.H. Hung, C.S. Yuan, Kinetic modeling of promotion and inhibition of temperature on photocatalytic degradation of benzene vapour, J. Photochem. Photobiol. 170 (2005) 299–306.
- [10] K. Okamoto, Y. Yamamoto, H. Tanaka, Kinetics of heterogeneous photocatalytic decomposition of phenol over anatase TiO₂ powder, Bull. Chem. Soc. 58 (1985) 2023–2028.
- [11] K. Kakinoki, K. Yamane, R. Teraoka, M. Otsuka, Y. Matsuda, Effects of relative humidity on the photocatalytic oxidation activity of titanium dioxide and photostability of formaldehyde, J. Pharm. Sci. 93 (2004) 582–589.
- [12] R.W. Matthews, S.R. McEvoy, A comparison of 254 nm and 350 nm excitation of TiO₂ in simple photocatalytic reactors, J. Photochem. Photobiol. A: Chem. 66 (1992) 355–366.