

Photocatalytic degradation of NO_x gases using TiO₂-containing paint: A real scale study

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Abstract

An indoor car park was appropriately equipped in order to test the de-polluting efficiency of a TiO₂-containing paint in an indoor polluted environment, under real scale configuration. Depollution tests were performed in an artificially closed area of the parking, which was polluted by a car exhaust during the testing period. The ceiling surface of the car park was covered with white acrylic TiO₂-containing paint (PP), which was developed in the frame of the EU project ‘PICADA’ (Photocatalytic Innovative Coverings Application for Depollution Assessment). The closed area was fed with car exhaust gases. As soon as the system reached steady state, the UV lamps were turned on for 5 h. The difference between the final and the initial steady state concentration indicates the removal of the pollutants due to both the photocatalytic paint and car emission reduction. Results showed a significant photocatalytic oxidation of NO_x gases. The photocatalytic removal of NO and NO₂ was calculated to 19% and 20%, respectively, while the photocatalytic rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) ranged between 0.05 and 0.13 for NO and between 0.09 and 0.16 for NO₂.

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1. Introduction

Advanced oxidation technologies represent emerging environmental control option for efficient removal of chemical pollutants. Among the various semiconductors TiO₂ in the form of anatase has attracted wide interest, due to its strong oxidizing power under UV irradiation, its chemical stability and the absence of toxicity [1].

The development of innovative materials that can be easily applied on facades, with both de-soiling and de-polluting properties, would be a significant step towards the improvement of air quality. The use of TiO₂ photocatalyst in combination with cementitious and other construction materials has shown a favorable synergetic effect in the removal of air pollutants [2]. In recent years, a wide number of laboratory scale tests have been performed, under different experimental conditions, in order to evaluate the de-polluting properties of TiO₂ photocatalytic materials [3–6]. Accordingly, some local governments of cities that

suffer from NO_x pollution like Tokyo and Osaka have started evaluating the performance of photocatalytic air-purifying materials on larger scales. Field tests shows that building materials, which can be used for applications such as in roadway structures or as outer materials on buildings, could achieve passive air purification [7].

In the frame of PICADA project (Photocatalytic Innovative Coverings Application for Depollution Assessment) such materials were developed and their photocatalytic de-polluting performances were evaluated through laboratory and real scale test methods [8–11]. For the purpose of this study, a car park was appropriately equipped for testing the depollution efficiency of a ‘PICADA’ TiO₂-containing paint in an indoor polluted environment, under real scale configuration.

2. Materials and methods

2.1. Description of the site configuration

A corner of the parking area was artificially closed in order to control pollution level, ventilation and measurements. Depollution tests were performed in the 917 m³ closed area, which was polluted by a car during the testing period. The

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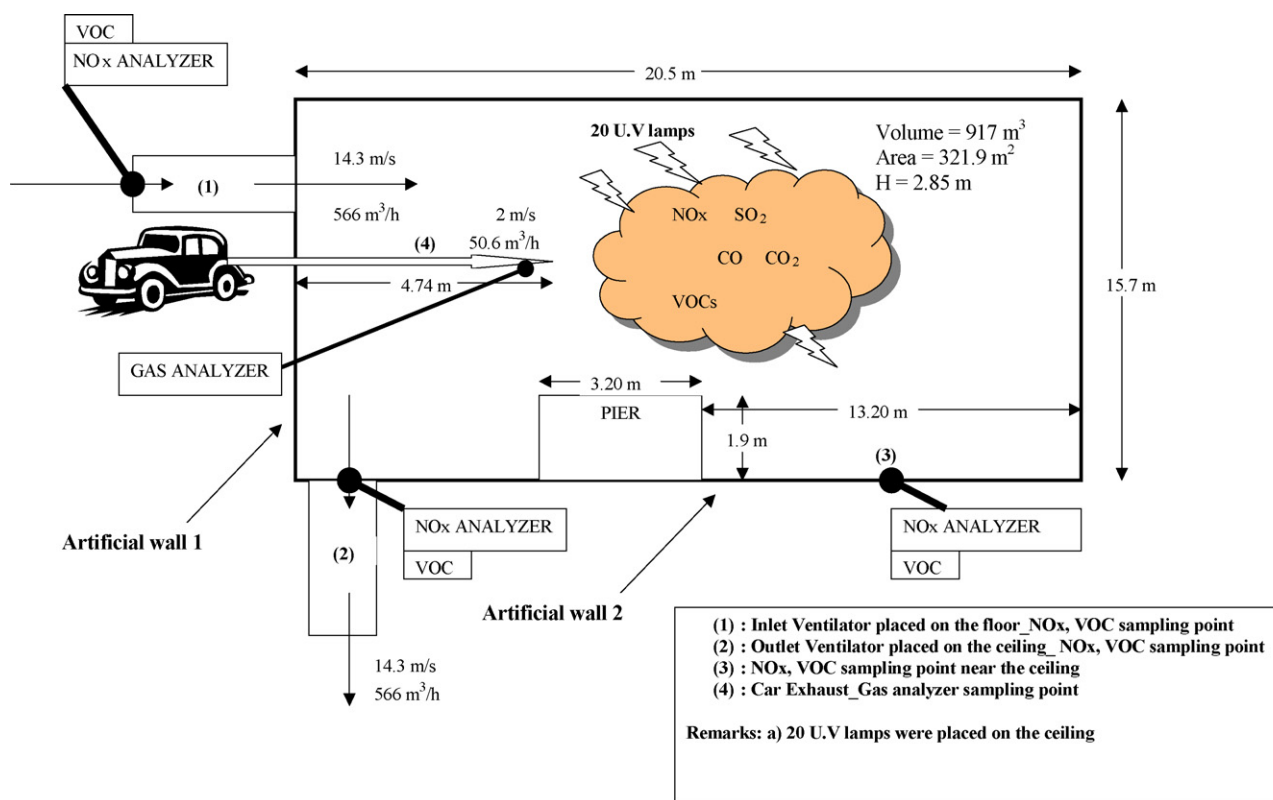


Fig. 1. Experimental site description.

322 m² ceiling surface of the car park was covered with white acrylic paint treated with 10% TiO₂ provided by Millennium Chemicals. Illumination was provided by 20 UV lamps (MAZDA/36 W/2500 lm), which were fixed symmetrically, 40 cm from the ceiling. The UVA and UVB intensity of each lamp was 144 and 13 mW/lm, respectively. The total UV irradiance near the active surface (ceiling) was measured 1 W m⁻². The car was placed outside the test area; its exhaust was connected to a pipe in order to release exhaust gases 4.7 m inside the closed area. Two ventilators (T VEC 3) of the same type (inlet and outlet) were suitably located on the artificial walls in order to achieve the highest concentrations of pollutants on the roof (active) area. Inlet and outlet ventilators were placed at the lowest level near the left corner of the 'Artificial wall 1' and at the highest level near the left corner of the 'Artificial wall 2', respectively (Fig. 1)

2.2. In situ instrumentation

Exhaust car gases (NO_x, SO₂, CO and CO₂) were continuously measured during each experiment using a HORIBA PG-250 portable gas analyzer. Continuous NO_x measurements were performed in the inlet and outlet ventilators, as well in a third sampling point near the 'PICADA wall 2' using AC32M Environment s.a NO_x chemiluminescence's analyzers.

Volatile organic compounds (VOCs) samples were collected during the experimental campaigns at the above-mentioned sampling points using Tenax-TA glass tubes. The analysis of the VOCs was performed in a thermal desorption unit (Chrompack)

coupled to a Gas Chromatograph (Hewlett-Packard, 5890, series II) using a flame ionization detector [12].

Airflow and gas velocity were measured in both inlet and outlet ventilators using a FLOWTEST TCR TECORA flowmeter. Calibration of all instruments was performed on site and according to the calibration and maintenance protocol based on the instructions manual of each instrument.

2.3. Duration

Three tests were performed under the above-described conditions as well as one blank (without UV irradiance). A working day was approximately organized as follows:

- Stage 1: Instruments calibration ventilators airflow measurements
- Stage 2: Car engine on (VOC sampling in both inlet and outlet ventilators)
- Stage 3: As soon as the system reached the steady state (approximately 3 h) the UV lamps were turned on (except blank experiment) (VOC sampling in both inlet and outlet ventilators)
- Stage 4: As soon as the system reached the steady state the UV lamps were turned off, car engine off as well (VOC sampling in both inlet and outlet ventilators)

During the engine working hours the exhaust gas composition was measured on 15 min basis, while continuous NO_x measurements were performed in both inlet and outlet ventilators.

Table 1
Exhaust gas chemical composition during the experimental days

	NO _x (ppm)	SO ₂ (ppm)	CO (ppm)	CO ₂ (vol.%)	O ₂ (vol.%)
First experiment					
Avg	29.3	0.42	222	2.68	14.9
Max	50.0	1.10	334	3.30	15.2
Min	16.4	0.10	141	2.48	14.1
Second experiment					
Avg	13.9	0.56	276	2.06	16.3
Max	20.0	1.70	665	2.38	19.9
Min	8.10	0.30	173	1.89	15.0
Third experiment					
Avg	26.8	0.38	159.5	2.29	15.9
Max	35.7	0.50	220.0	2.53	16.5
Min	21.2	0.10	96.00	2.16	10.1
BLANK					
Avg	30.0	0.60	256.6	3.21	15.0
Max	41.4	1.00	357.0	3.54	15.2
Min	21.3	0.10	129.0	3.07	14.5

3. Results and discussion

3.1. Evaluation of pollution source impact

Gas chemical composition (NO, NO_x, SO₂, CO, CO₂, O₂) and kinetic characteristics were measured during each experiment in the exhaust pipe. Statistical analysis of the measured values is presented in Table 1.

Table 1 shows that gas emissions from the car were not stable during the experiment as well as between the experimental days. The variation of NO_x gases could more clearly be seen in Fig. 2. Specifically, NO emission was reduced during the experiment, while the CO was increased (Fig. 3). The measurement of NO_x emissions reduction is essential due to the fact that the measurement of the photocatalytic properties of the material is based on the elimination of NO_x during the irradiation time. For that purpose it was important to measure the NO_x reduction during the experimental time due to car exhaust gas variations.

Airflow and velocity of car gas exhaust reached 50.6 m³ h⁻¹ and 2 m s⁻¹, respectively. On the other hand, the corresponding

values for ventilator's airflow and velocity were 566 m³ h⁻¹ and 14.3 m s⁻¹, respectively. In that way an overpressure was established in the closed area in order to avoid the inflow of outdoor air.

3.2. Evaluation of TiO₂-paint photocatalytic efficiency on NO_x

The closed area was fed with car exhaust gases. As soon as the system reached steady state (approximately 3 h), the UV lamps were turned on for 5 h.

The difference between the final and the initial (steady state) concentration indicates the removal of the pollutants due to: (a) photocatalytic paint and (b) car emission reduction. The subtraction of car emission reduction from the total removal consists an indication of the photocatalytic removal of the pollutants (Tables 2 and 3) and was calculated by the following equations:

$$\%NO_x = \left(\frac{[NO_x]_{in} - [NO_x]_{UV}}{[NO_x]_{in}} \times 100 \right) - \%NO_x \quad (1)$$

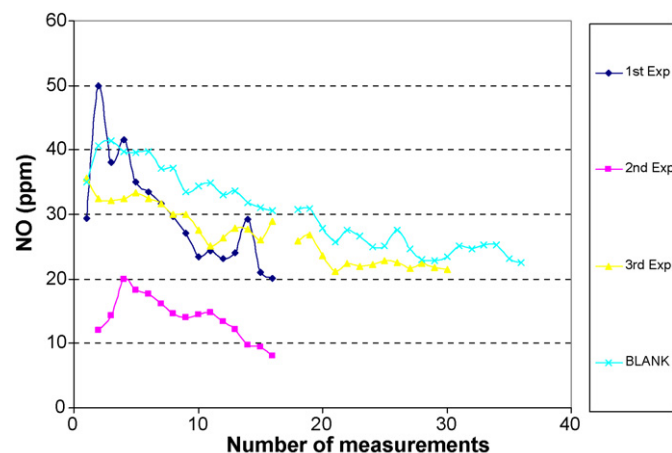


Fig. 2. NO (ppm) car exhaust variation during experiments.

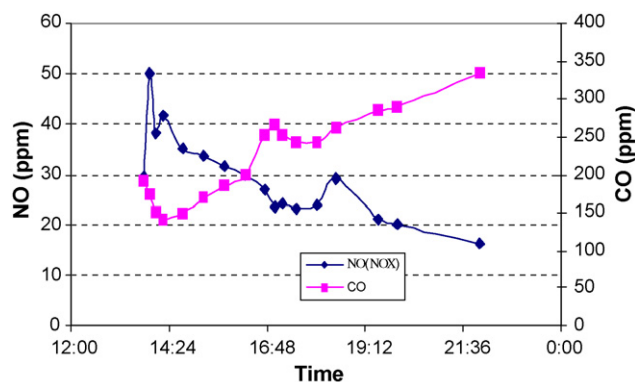


Fig. 3. NO_x (ppm) and CO (ppm) car exhaust variation during an experimental day.

Table 2
%NO photocatalytic oxidation during the experimental days

Experimental day	Initial NO concentration (steady state) ($\mu\text{g m}^{-3}$)	UV irradiation time (h)	Final NO concentration ($\mu\text{g m}^{-3}$)	%NO total removal	%NO reduction due to car emission reduction	%NO oxidation due to TiO_2 + UV
1	1365	5	726	46.8	28	18.8
2	779	5	439	43.6	28	15.6
3	1607	4	1122	30.2	23.5	6.67
4 (BLANK)	1439	0	1036	28 (5 h)	28 (5 h)	0
			1100	23.5 (4 h)	23.5 (4 h)	

Initial NO steady state concentration, final NO concentration after the irradiation procedure and contribution of the car emission reduction to final NO concentration.

Table 3
%NO₂ photocatalytic oxidation during the experimental days

Experimental day	Initial NO ₂ concentration (steady state) ($\mu\text{g m}^{-3}$)	UV irradiation time (h)	Final NO ₂ concentration ($\mu\text{g m}^{-3}$)	%NO ₂ total removal	%NO ₂ reduction due to car emission reduction	%NO ₂ oxidation due to TiO_2 + UV
1	1704	5	1452	14.8	0	14.8
2	1679	5	1352	19.4	0	19.4
3	2145	4	1965	8.37	0	8.37
4 (BLANK)	2141	0	2133	0	0	0

Initial NO₂ steady state concentration, final NO₂ concentration after the irradiation procedure and contribution of the car emission reduction to final NO₂ concentration.

where

$$\%NO_x = \frac{\text{BLANK}[NO_x]_{\text{in}} - \text{BLANK}[NO_x]_{\text{fin}}}{\text{BLANK}[NO_x]_{\text{in}}} \times 100 \quad (2)$$

$[NO_x]_{\text{in}}$ is the initial steady-state pollutant concentration (before turn on the UV source), $[NO_x]_{\text{UV}}$ the pollutant concentration during irradiation phase, $\text{BLANK}[NO_x]_{\text{in}}$ the initial steady state pollutant concentration, and $\text{BLANK}[NO_x]_{\text{fin}}$ is the pollutant concentration at the end of the blank experiment (without irradiation).

The main conclusion from the above tables is that NO reduction during experimental campaigns was significantly affected by the elimination of car engine NO emissions while NO₂ does not seem to be affected by the variations of car gas emissions. However, a significant amount of both pollutants were photocatalytically removed during tests. It was calculated that up to 18.8% and 19.4% of NO and NO₂, respectively, were photocatalytically removed.

The photocatalytic oxidation rate of the tested material for NO and NO₂ was calculated with the following equation:

$$\text{photo-oxidation rate (PR)} = \frac{[NO_x]_{\text{TiO}_2\text{-UV}}}{A} \times F \quad (3)$$

where (PR) is the photo-oxidation rate ($\mu\text{g m}^{-2} \text{s}^{-1}$), $[NO_x]_{\text{TiO}_2\text{-UV}}$ the pollutant concentration ($\mu\text{g m}^{-3}$) removed by the TiO₂ effect, F is the airflow of ventilator ($\text{m}^3 \text{h}^{-1}$), and A is the sample area exposed to the irradiation (m^2).

Additionally, the photocatalytic activity (cm s^{-1}) was calculated (Eq. (4)) in order to describe the photocatalytic activity of the material with a non-concentration-dependent parameter.

$$\text{photocatalytic activity (PA)} = \frac{\text{PR}}{([NO_x]_{\text{in}} + [NO_x]_{\text{uv}})/2} \quad (4)$$

where PA is the photocatalytic activity (cm s^{-1}), PR the photocatalytic rate ($\mu\text{g m}^{-2} \text{s}^{-1}$), $[NO_x]_{\text{in}}$ the pollutant initial steady state concentration $\mu\text{g m}^{-3}$ (before turn on the UV source),

and $[NO_x]_{\text{UV}}$ is the pollutant concentration ($\mu\text{g m}^{-3}$) during irradiation phase.

Table 4 presents the NO and NO₂ photocatalytic parameters during the tests. The lowest photocatalytic consumption for both pollutants was presented during the third day test. Excluding that day, PR for NO and NO₂ ranged between 0.06 and 0.13 $\mu\text{g m}^{-2} \text{s}^{-1}$ and between 0.12 and 0.16 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively, while PA was calculated 0.01 cm s^{-1} for both pollutants.

Fig. 4 represents the variation of NO during the experiment. During the blank test reduction of NO was observed due to car exhaust emission elimination. However, it can be seen that the NO removal during UV experiments (1–3) is higher than the blank, indicating the photocatalytic effect of the material. From Fig. 5 it is obvious that as soon as the UV was turned on, the NO₂ concentration was significantly reduced due to TiO₂ effect. According to the blank experiment, engine gas emissions variation does not seem to affect NO₂. As soon as NO₂ reached the steady state it remained steady although NO emissions from the

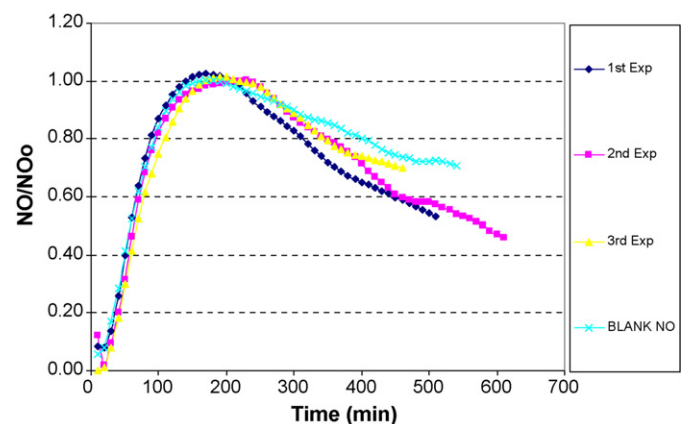


Fig. 4. NO/NO_o variation during the experiments (NO_o is the concentration in the steady state).

Table 4
NO and NO₂ photocatalytic parameters (%removal, photocatalytic rate $\mu\text{g m}^{-2} \text{s}^{-1}$, photocatalytic activity cm s^{-1})

Test day	NO			NO ₂		
	%photo-removed	PR ($\mu\text{g m}^{-2} \text{s}^{-1}$)	PA (cm s^{-1})	%photo-removed	PR ($\mu\text{g m}^{-2} \text{s}^{-1}$)	PA (cm s^{-1})
1	18.8	0.13	0.012	14.8	0.12	0.008
2	15.6	0.06	0.009	19.4	0.16	0.011
3	6.67	0.05	0.004	8.37	0.09	0.004
4 (BLANK)	0	0	0	0	0	0

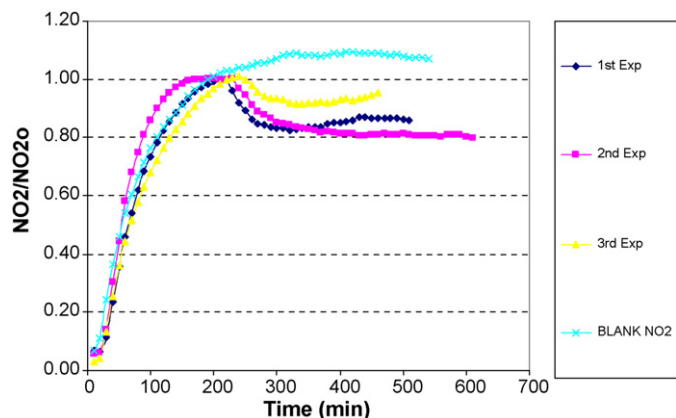


Fig. 5. NO₂/NO_{2o} variation during the experiments (NO_{2o} is the concentration in the steady state).

engine were reduced. In this case, the observation of the photocatalytic oxidation of NO₂ was more clear than NO. In both cases (Figs. 4 and 5), the NO_x concentrations were divided by the initial concentration in order to be able to compare results of each experiment on the same basis.

3.3. Lab scale evaluation of material photocatalytic properties

In order to evaluate results from the real scale study, the same material was tested in a 30 m³ stainless steel environmental chamber under controlled environmental conditions. Two hundred and twenty parts per billion NO were injected in the environmental chamber, where 4 m² of the TiO₂-material was placed. Illumination was provided by four UV lamps, which were mounted on the ceiling 1.5 m above the samples' surface. UV light intensity measurements were performed on three different points (centre, diagonal and corner) on the surface of the material, with a radiometer DELTA-OHM mod. HD9021, with UVA and UVB probes mod. LP9021 (range: UVA 315–400 nm,

Table 5
Mean values ($\mu\text{g m}^{-3}$) during the experimental days, measured at the outlet ventilator

Experimental day	Benzene mean concentration ($\mu\text{g m}^{-3}$) (number of samples: 4)	Toluene mean concentration ($\mu\text{g m}^{-3}$) (number of samples: 4)	<i>m</i> + <i>p</i> -Xylene mean concentration ($\mu\text{g m}^{-3}$) (number of samples: 4)	<i>o</i> -Xylene mean concentration ($\mu\text{g m}^{-3}$) (number of samples: 4)
First	23.7	23.7	10.4	4.80
Second	84.3	71.8	25.4	15.6
Third	93.3	109	35.4	14.7
Fourth	67.7	82.5	31.9	12.9

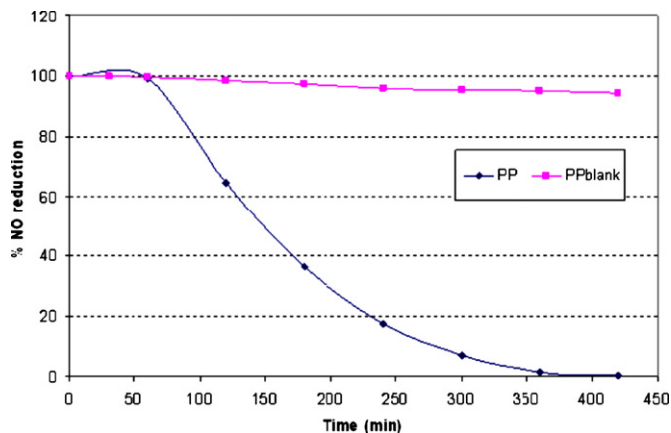


Fig. 6. %NO removal during laboratory scale experiments.

UVB 280–315 nm). It was found that the UVA irradiance ranged between 0.12 and 4.72 W m⁻², while measuring on the corner and the centre of samples' surface, respectively. Detailed description of the lab scale experimental conditions and methodology is given in Maggos et al. [9]. Fig. 6 shows the elimination of NO due to the TiO₂-containing material photocatalytic effect as well as from the corresponding blank (same material without TiO₂). It was calculated that 91.3% of NO were photocatalytically removed due to TiO₂ effect after 6 h of irradiation, while the values for the photocatalytic rate and the photocatalytic activity were calculated 0.18 $\mu\text{g m}^{-2} \text{s}^{-1}$ and 0.13 cm s^{-1} , respectively.

Results from the above experiment indicate better photocatalytic behavior of the material under laboratory than real scale experiments. It is well known that the variation of temperature, relative humidity (RH) and mixture of chemical compounds could have significant effect on the efficiency of a photocatalytic material [13,14]. Additionally, the presence of VOCs such as benzene, toluene, xylenes, etc. could have inhibition effect on NO_x photocatalytic oxidation due to the competition of the pollutants for OH radicals and for absorption sites on the cata-

lysts' surface [3,15,16]. During the laboratory scale tests NO (or NO₂) was the only pollutant in the chamber, while during the real scale the presence of VOCs were significant. In particular, benzene, toluene, *m* + *p*-xylene and *o*-xylene concentration during the experimental days ranged between 23.7 and 93.3, 23.7 and 82.5, 10.4 and 35.4 and 4.80 and 15.6 μg m⁻³, respectively. The unstable environmental conditions (*T* (°C), RH (%)) and the presence of VOCs in the system (Table 5) could be the main factors for the elimination of the photocatalytic oxidation of NO during the car park experiment.

4. Conclusions

A car park was chosen to evaluate the indoor depollution efficiency of a TiO₂-containing paint. The experimental site was polluted by car exhaust gases, while the ventilation of the site was controlled by means of two same type ventilators. The TiO₂-containing photocatalytic paint, which was applied on the ceiling of the car park, was activated by 1 W cm⁻² irradiation provided by 20 UV lamps. Taking into account the reduction of the pollution due to the car emission variation, the photocatalytic removal of NO and NO₂ was about 19% and 20%, respectively, while the corresponding photocatalytic rate (μg m⁻² s⁻¹) ranged between 0.05 and 0.13 and between 0.09 and 0.16. The photocatalytic activity of the paint for NO and NO₂ was calculated to 0.012 and 0.011 cm s⁻¹, respectively.

The same material was tested in an environmental chamber, under strictly controlled environmental conditions. NO (or NO₂) was the only pollutant in the chamber, while the temperature and the relative humidity were set at 23 °C and 20%, respectively. The photocatalytic rate was calculated 0.18 μg m⁻² s⁻¹ for NO, which indicates better photocatalytic behavior of the material under laboratory scale experiments. The controlled and less complicated environmental conditions of a lab scale test result to less inhibition effects, which usually lead to an over-estimation of the photocatalytic capacity of a TiO₂-containing material. For example, the presence of organic pollutants in real world has inhibition effect on the photocatalytic efficiency of the paint to oxidize NO_x. Nevertheless, in the present study it was shown that beyond the laboratory studies, the photocatalytic paint could be active in real scale. The results presented at the above real scale test showed that heterogeneous photocatalysis could be used as a tool for the improvement of air quality.

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References

- [1] H. Ibrahim, H. Lasa, Photocatalytic conversion of air borne pollutants effect of catalyst type loading in a novel photo-CREC-air unit, *Appl. Catal. B: Environ.* 38 (2002) 201–213.
- [2] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, BKC, Inc., Japan, 1999.
- [3] 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.
- [4] S. Devahashdin, 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.
- [5] 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.
- [6] 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.
- [7] M. Kaneko, I. Okura, *Photocatalysis Science and Technology*, Springer/Kodansha, New York/Tokyo, 2002.
- [8] N. Allen, M. Edge, J. Stratton, R. McIntyre, Photoactivity of titanium dioxide nanoparticles in polymers and coatings, in: *Proceedings of the Conference on Polymer Materials in the Environment and Minerals*, Bejaia, Algeria, September 10–11, 2003.
- [9] Th. Maggos, D. Kotzias, J. Bartzis, P. Leva, A. Bellintani, Ch. Vasilakos, Investigations of TiO₂-containing construction materials for the decomposition of NO_x in environmental chambers, in: *Proceedings of the 5th International Conference on Urban Air Quality*, Valencia, Spain, March 29–31, 2005, p. 68.
- [10] N. Moussiopoulos, I. Ossanlis, Ph. Barbas, J. Bartzis, Comparison of numerical and experimental results for the evaluation of the depollution effectiveness of photocatalytic coverings in street canyons, in: *Proceedings of Fifth International Conference on Urban Air Quality*, Valencia, Spain, March 29–31, 2005, p. 70.
- [11] A. Strini, S. Cassese, L. Schiavi, Measurement of benzene, toluene, ethylbenzene and *o*-xylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor, *Appl. Catal. B: Environ.* 61 (2005) 90–97.
- [12] A. Papadopoulos, Ch. Vasilakos, J. Hatzianestis, Th. Maggos, J. Bartzis, Volatile organic compounds concentration levels on a day without traffic in the center of Athens, *Fresen. Environ. Bull.* 14 (2005) 498–502.
- [13] J. Zhao, X. Yang, Photocatalytic oxidation for indoor air purification: a literature review, *Build. Environ.* 38 (2003) 645–654.
- [14] J.M. Hermann, Heterogeneous photocatalysis: an emerging discipline involving multiphase systems, *Catal. Today* 24 (1995) 157–164.
- [15] C.H. Ao, S.C. Lee, Comination effect of activated carbon with TiO₂ for the photodegradation of binary pollutants at typical indoor air level, *J. Photochem. Photobiol. A: Chem.* 161 (2004) 131–140.
- [16] C.H. Ao, S.C. Lee, S.C. Zou, C.L. Mak, Inhibition effect of SO₂ on NO_x and VOCs during the photodegradation of synchronous indoor air pollutants at parts per billion (ppb) level by TiO₂, *Appl. Catal. B: Environ.* 49 (2004) 187–193.