Catalysis Today 161 (2011) 175–180

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Experimental study of the NO and NO_2 degradation by photocatalytically active concrete

M.M. Ballari*, Q.L. Yu, H.J.H. Brouwers

Unit of Building Physics and Systems, Department of Architecture, Building and Planning, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:
Available online 11 November 2010

Keywords:
Heterogeneous photocatalysis
Atmospheric reactions
NO and NO_2
Air purification
Concrete pavement

ABSTRACT

The application of photocatalytic concrete containing TiO_2 in urban streets is a method to improve the air quality in highly polluted areas. By using this technology it is possible to degrade a wide range of air contaminants, like nitric oxide (NO) and nitrogen dioxide (NO_2), mainly emitted by automobiles. In the present paper, the photocatalytic degradation of NO and NO_2 is experimentally studied, and the atmospheric reactions involving nitrogen oxides and solar radiation are analyzed as well. In addition, the influence of different system parameters, such as inlet pollutant concentration, relative humidity, and irradiance is investigated in detail.

1. Introduction

Heterogeneous photocatalytic oxidation is a promising and sustainable technology to be applied to water and air purification. This process applies a solid semiconductor catalyst, normally titanium dioxide (TiO_2), which is activated by ultraviolet (UV) light of certain wavelength. The main advantages of this technology are: (i) pollutants can be completely transformed into innocuous products, and (ii) a wide range of contaminants can be treated due to its very low selectivity.

Nowadays, nitrogen oxides (NO_x) represent a serious environmental problem in highly contaminated areas. Nitrogen oxides (mainly NO and NO_2) are produced during fuel burning processes, for example in automobiles, causing a wide variety of health and environmental impacts, like the formation of tropospheric ozone and urban smog through photochemical reactions with hydrocarbons. Furthermore, NO_x together with SO_x (sulfur dioxide and sulfur trioxide) are the major contributors to the “acid rain”.

One of the European Union (EU) directives (1999/30/EC) [1] established limit values for concentrations of the most representative air pollutants. However, NO_x exceeds the maximum allowed limit, especially in urban areas (e.g. in the Randstad conurbation, the Netherlands [2]), and extra measures are needed to solve this problem. The application of TiO_2 in concrete pavement has shown a promising effect in the removal of nitrogen oxides and attempts to improve the air quality in urban streets [3–5].

Currently, there are some international and national standards available to assess the photocatalytic oxidation efficiency of semiconducting materials. Some of them employ only NO as the target pollutant [6], while others use a mixture of NO and NO_2 to perform the test [7,8]. However, since the test is carried out in the presence of light, not only photocatalytic reactions take place but also homogeneous and photolysis reactions of NO_x occur, but so far, no research has linked this to their photocatalytic oxidation.

In the present paper, the photocatalytic degradation of NO and NO_2 is experimentally studied and the homogeneous reactions involving NO_x are analyzed employing a photocatalytic concrete stone, and a normal non-active concrete block as a blank sample. In addition, the influence of different system parameters, such as inlet pollutant concentration, relative humidity, and irradiance is investigated. Depending on the employed operating conditions, part of the NO_x conversion employing the photocatalytic stone corresponds to homogeneous reactions under UV light [9], but not just to photocatalytic reactions alone.

2. Experimental

The applied experimental set-up is composed of a continuous planar reactor housing the concrete stone sample, a suitable UV-A light source, a chemiluminescent NO_x analyzer, and an appropriate gas supply system for NO and NO_2 (Fig. 1). Table 1 shows the main characteristics, dimensions and operating conditions of the test setup employed to execute the NO_x degradation experiments.

To carry out the experiments, one photocatalytic and one normal commercial paving stone samples were used. The employed photocatalytic sample is a double layer stone with the upper layer being photocatalytically active. This upper layer is prepared by mixing

---

* Corresponding author. Tel.: +31 40 2472195; fax: +31 40 2438595.
E-mail address: m.ballari@tue.nl (M.M. Ballari).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.09.028

Nomenclature

A	Area (dm^2)
B	Reactor width (dm)
C	Concentration (ppm)
E	Radiative flux ($W\,m^{-2}$)
H	Reactor height (dm)
L	Reactor length (dm)
Q	Flow rate ($l\,min^{-1}$)
RH	Relative humidity (%)
t	Time (min)
V	Reactor volume (dm^3)

Subscripts

in	Inlet condition
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
out	Outlet condition

Table 1
Experimental setup main characteristics and operating conditions.

Description	Operating conditions
Reactor	
Length (L)	2 dm
Width (B)	1 dm
Height (H)	0.03 dm
Volume (V)	0.06 dm^3
Photocatalytic/blank concrete stone	
Length (L)	2 dm
Width (B)	1 dm
UV Lamps: Philips Compact S × 3	
Input power	25 W
Emission wavelength	300–400 nm
Flow rate (Q)	3 $l\,min^{-1}$
Relative humidity (RH)	10–70%
Irradiance flux (E)	2–11 $W\,m^{-2}$
NO inlet concentration ($C_{NO,in}$)	0–1 ppm
NO_2 inlet concentration ($C_{NO_2,in}$)	0–1 ppm

dry powders of normal concrete with TiO_2 powder before adding water. According to X-ray fluorescence (XRF) analysis performed in the upper layer of the stone, the present concrete sample has a TiO_2 content of 5.9% by weight. In preparation of each experiment, the sample surface is washed with water in order to remove fouling, contamination and potential reaction products due to a previous NO_x degradation.

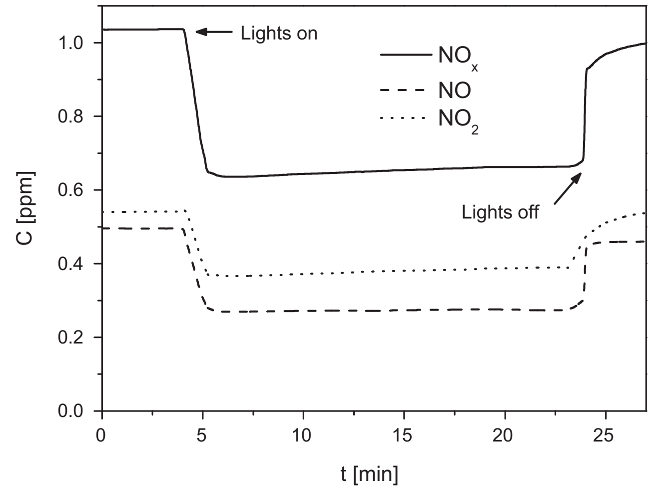

Fig. 2. Representative experimental result. $H = 3$ mm, $Q = 3\,l\,min^{-1}$, $C_{NO_2,in} \sim 0.5$ ppm, $C_{NO,in} \sim 0.5$ ppm, $E = 10\,W\,m^{-2}$ and RH = 50%.

After assembling the sample the reactor is closed and the gas supply is started. The UV-A source is switched on as well in order to stabilize the radiation, but the reactor stays covered to prevent the first degradation. With the help of the controls, the flow rate and the relative humidity are adjusted. The supplied NO/NO_2 concentration is adjusted to the desired inlet concentration, which is monitored by the analyzer. When these conditions are stable the data acquisition is started. After this period of time, the reactor cover is removed to allow the UV-radiation passing through the glass. The degradation for the uncovered reactor lasts for 20 min, then the reactor is covered again and the experiment is continued for another 5 min. Within the last minutes of measurement the NO and NO_x concentrations return ideally to the original scale. An example of a representative experimental result is shown in Fig. 2, where the different steps mentioned above and the degradation of NO and NO_2 can be observed.

3. Results

Table 2 shows the results of NO/NO_2 conversion and the operating conditions employed in every performed experiment. In this table, four types of experiments are listed: (i) experiments feeding only NO to the system; (ii) experiments employing only NO_2; (iii) experiments employing a mixture of NO and NO_2, and (iv) blank experiments using a non-photocatalytic sample. Within these groups, different experiments were carried out by varying the inlet concentration of NO or NO_2 and operating conditions of irradiance and relative humidity.

Figs. 3–7 show the obtained results under different operating conditions. Figs. 3–5 show the experimental results of NO and NO_2 outlet concentration with varying the inlet concentration of the pollutants, the relative humidity and the irradiance when NO, NO_2

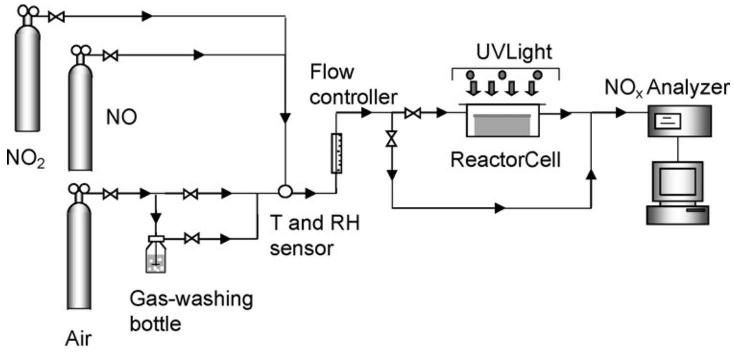

Fig. 1. Schematic representation of the experimental setup.

Table 2
Experimental results of the photocatalytic NO_x degradation under different operating conditions.

	Experiment #	HR (%)	E ($W\,m^{-2}$)	$C_{NO,in}$ (ppm)	$C_{NO,out}$ (ppm)	$C_{NO_2,in}$ (ppm)	$C_{NO_2,out}$ (ppm)	NO conversion (%)	NO_2 conversion (%)	NO_x conversion (%)
	1	50.0	10.0	1.01	0.57	0.00	0.08	43.3	−14,313.0	34.9
	2	50.4	10.0	0.49	0.19	0.00	0.05	61.8	−5154.8	51.3
	3	50.0	10.2	0.11	0.02	0.00	0.01	82.9	−1561.7	71.8
	4	10.2	10.1	0.52	0.06	0.00	0.02	89.2	−1813.9	84.6
	5	30.5	10.1	0.52	0.14	0.00	0.05	72.7	−3627.7	63.9
	6	49.2	10.1	0.52	0.22	0.00	0.05	57.2	−4319.9	46.8
	7	69.0	10.1	0.52	0.26	0.00	0.06	49.0	−4636.5	37.9
	8	49.6	10.9	0.52	0.22	0.00	0.04	57.6	−7493.7	49.9
	9	49.4	10.0	0.52	0.25	0.00	0.05	51.1	−8982.2	41.9
	10	50.5	8.1	0.52	0.29	0.00	0.05	44.2	−8902.2	35.1
	11	50.0	6.0	0.52	0.32	0.00	0.04	37.5	−8194.7	29.1
	12	49.6	4.1	0.52	0.37	0.00	0.04	29.2	−6769.0	22.3
	13	50.7	2.1	0.52	0.42	0.00	0.03	19.8	−4676.3	15.1
	14	49.8	10.0	0.06	0.12	0.99	0.54	−109.2	45.2	36.5
	15	49.8	10.0	0.08	0.06	0.50	0.24	28.0	51.6	48.5
	16	49.7	10.0	0.07	0.02	0.12	0.05	69.2	59.5	63.2
	17	10.1	10.0	0.09	0.04	0.50	0.13	55.1	75.1	72.1
	18	29.9	10.0	0.04	0.04	0.51	0.24	9.8	52.5	49.1
	19	50.0	9.9	0.06	0.06	0.49	0.29	11.2	40.8	37.3
	20	64.4	10.0	0.05	0.07	0.47	0.38	−40.9	19.8	13.8
	21	50.0	10.7	0.06	0.06	0.49	0.28	11.5	42.6	39.0
	22	50.0	9.9	0.06	0.06	0.49	0.29	11.2	40.8	37.3
	23	49.4	8.0	0.06	0.06	0.49	0.32	10.7	35.9	32.9
	24	49.3	6.0	0.06	0.06	0.49	0.35	9.9	29.6	27.4
	25	50.1	3.9	0.06	0.06	0.49	0.37	9.1	23.9	22.2
	26	49.8	2.1	0.06	0.06	0.49	0.41	11.4	16.2	15.6
	27	49.9	12.1	0.50	0.24	0.54	0.32	51.4	40.7	45.8
	28	49.9	10.3	0.50	0.27	0.54	0.38	44.9	30.5	37.4
	29	49.8	8.0	0.50	0.31	0.54	0.41	38.0	23.4	30.4
	30	49.9	6.0	0.50	0.34	0.54	0.45	32.2	17.0	24.2
	31	49.8	4.2	0.50	0.36	0.54	0.47	27.5	12.7	19.8
	32	49.6	2.1	0.50	0.40	0.54	0.50	18.5	7.1	12.6
	33	68.7	10.1	0.49	0.37	0.54	0.62	24.1	−14.4	3.9
	34	67.9	6.0	0.49	0.39	0.54	0.57	19.1	−6.4	5.7
	35	67.2	2.0	0.49	0.44	0.54	0.56	9.6	−3.7	2.6
	36	29.8	10.1	0.47	0.23	0.52	0.35	51.6	31.9	41.3
	37	30.2	6.0	0.47	0.30	0.52	0.41	35.0	21.9	28.1
	38	30.3	2.0	0.5	0.4	0.5	0.5	15.3	11.4	13.2
Blank	39	50.1	10.1	0.45	0.44	0.56	0.50	3.4	10.6	7.4
	40	49.7	10.0	0.54	0.52	0.01	0.01	4.4	−35.6	3.8
	41	50.2	10.1	0.06	0.06	0.47	0.43	−12.5	8.3	6.0

or both contaminants together are used respectively. When the inlet concentration of NO or NO_2 increases, both NO and NO_2 outlet concentration grows as well. However, as expected, when the inlet concentration of the pollutants is decreased, the final conversion of the reacting system increases. Regarding the irradiance and relative humidity effect, in all cases when the irradiance is increased a higher conversion of the pollutants is achieved. However, when the relative humidity is enlarged, the NO_x conversion declines.

Fig. 6 shows the comparison between the NO_x degradation achieved by employing a concrete stone containing TiO_2 and a normal stone without an active surface. Observing the obtained results with the non-active sample, NO_x is also degraded in the presence of UV light, which indicates the existence of homogeneous reactions.

Finally, Fig. 7 shows an overview how the irradiance and the relative humidity influence the degradation rate when both NO and NO_2 are fed to the system using a photocatalytic sample.

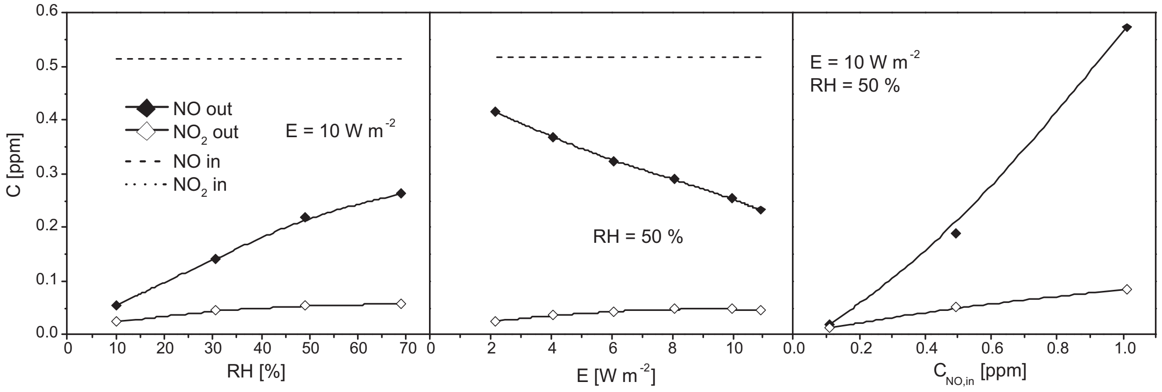

Fig. 3. NO and NO_2 outlet concentrations employing a photocatalytic concrete stone and varying the relative humidity, irradiance and inlet NO concentration. $C_{NO_2,in}$~0 ppm.

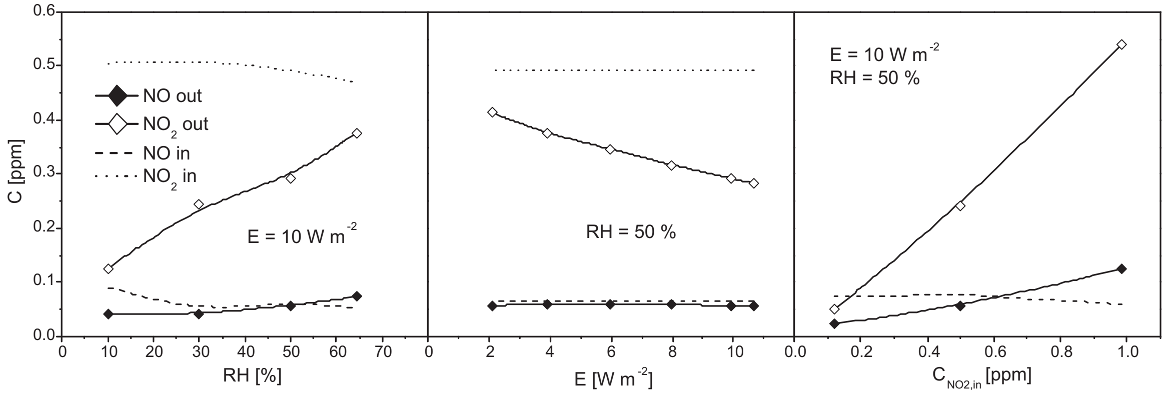

Fig. 4. NO and NO_2 outlet concentrations employing a photocatalytic concrete stone and varying the relative humidity, irradiance and inlet NO_2 concentration. $C_{NO,in} \sim 0$ ppm.

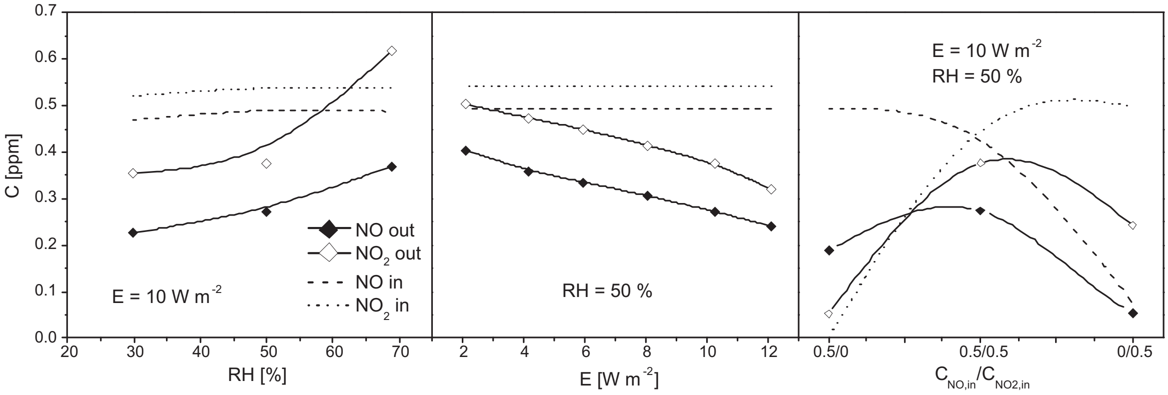

Fig. 5. NO and NO_2 outlet concentrations employing a photocatalytic concrete stone and varying the relative humidity, irradiance and inlet NO_2 and NO concentration ratio.

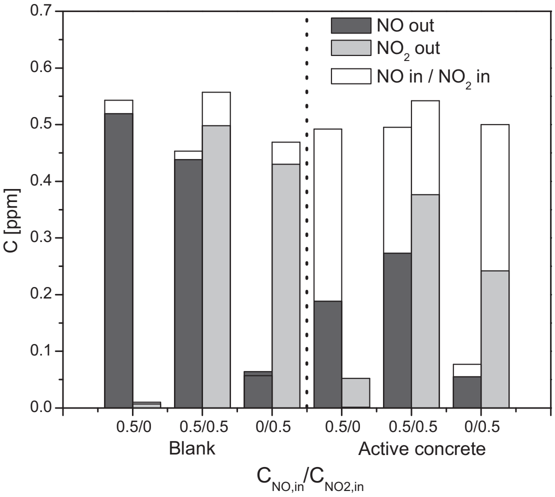

Fig. 6. NO and NO_2 outlet concentrations employing a photocatalytic concrete stone and a normal non-active concrete stone. RH = 50% and $E = 10\,W\,m^{-2}$.

4. Discussion

The photocatalytic oxidation mechanism of NO_x is reported in several publications (e.g. [10–13]). All of them proposed the NO oxidation to NO_2, and then NO_2 to HNO_3 due to the attack of the hydroxyl radical generated in the photocatalyst activation stage. The photocatalytic degradation process can be described by the following path:

Adsorption of the involved gas species over the active sites of TiO_2:

$$O_2 + \text{site} \rightarrow O_{2ads} \tag{1}$$

$$H_2O + \text{site} \rightarrow H_2O_{ads} \tag{2}$$

$$NO + \text{site} \rightarrow NO_{ads} \tag{3}$$

$$NO_2 + \text{site} \rightarrow NO_{2ads} \tag{4}$$

Activation of TiO_2 by generating holes and electrons:

$$TiO_2 + h\nu(\lambda < \sim 390\,\text{nm}) \rightarrow e^- + h^+ \tag{5}$$

Trapping of holes by water:

$$h^+ + H_2O_{ads} \rightarrow OH^\bullet + H^+ \tag{6}$$

Trapping of electron by oxygen:

$$e^- + O_{2ads} \rightarrow O_2{}^- \tag{7}$$

Contaminants attack by hydroxyl radical:

$$NO_{ads} + OH^\bullet \rightarrow HNO_2 \tag{8}$$

$$HNO_2 + OH^\bullet \rightarrow NO_{2ads} + H_2O \tag{9}$$

$$NO_{2ads} + OH^\bullet \rightarrow NO_3{}^- + H^+ \tag{10}$$

Recombination of electrons and holes:

$$e^- + h^+ \rightarrow \text{heat} \tag{11}$$

Nevertheless, observing the results obtained with the blank sample (Fig. 6), NO_x is also degraded in the presence of UV light, which indicates the occurrence of homogeneous reactions.

In the atmosphere a process takes place in which NO, NO_2 and O_3 are both formed and destructed. This process, which is called

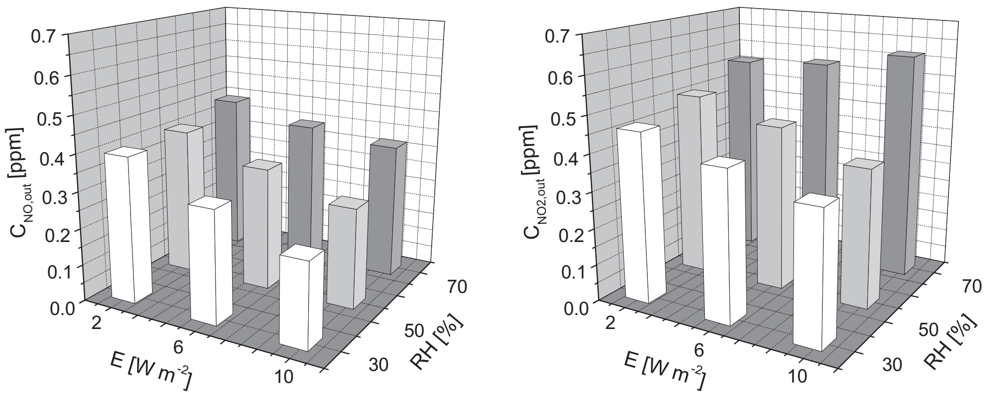

Fig. 7. Effect of the irradiance and relative humidity over the NO and NO_2 outlet concentration using a photocatalytic concrete stone. $C_{NO,in} \sim 0.5$ ppm and $C_{NO_2,in} \sim 0.5$ ppm.

the "Leighton cycle" [8], starts with photolysis of NO_2 under the influence of UV irradiance:

$$NO_2 + h\nu(\lambda < \sim 430\,\text{nm}) \rightarrow NO + O \quad (12)$$

The O-atoms created in this process then react instantaneously with O_2 to form O_3, and in an unpolluted atmosphere the NO reacts with O_3 to form NO_2 and O_2 again:

$$O + O_2 \rightarrow O_3 \quad (13)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (14)$$

In addition, NO_2 is also degraded by a reaction with O_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (15)$$

The final balance of these reactions is the depletion of NO_x into oxidized nitrogen products.

Analyzing the obtained results when only NO is fed to the photoreactor (Fig. 3), NO_2, an intermediate of the photocatalytic reaction, is generated in the system (Eq. (9)), especially when the inlet NO concentration is higher. This indicates that under these operating conditions, the photocatalytic reaction and also the homogeneous reactions cannot convert completely NO to nitrate. In addition, from Fig. 3 it is also possible to observe that when the irradiance is increased a higher conversion of NO_x is achieved. This is because more electrons and holes are produced during the photocatalyst activation stage (Eq. (5)) and therefore, more hydroxyl radicals are formed (Eq. (6)). On the other hand, when the relative humidity is increased, water competes with NO and NO_2 for the same active sites (Eqs. (2)–(4)) and the NO_x consumption declines.

According to the second type of experiments performed in this study employing only NO_2 as the pollutant, the same behavior when varying irradiance, relative humidity and inlet concentration was observed (Fig. 4). Nevertheless, the inlet concentration of NO in the reactor is not equal to zero. This occurs because NO_2 can react with the water vapor producing NO, as follows:

$$3NO_2 + H_2O \rightarrow NO + 2HNO_3 \quad (16)$$

However, for this group of experiments, in most cases NO is also degraded in the photoreactor, except when the inlet NO_2 concentration or the relative humidity is high (Fig. 4). In both cases, the homogeneous photolysis reaction of NO_2 producing NO (Eq. (12)) is more significant than the degradation photocatalytic steps. In the first case, the availability of NO_2 is high and therefore the photolysis of NO_2 is faster. On the other hand, when the relative humidity is high the photocatalytic degradation of NO is lower, so the apparition of this component becomes more significant.

When both contaminants NO and NO_2 are employed in the same proportion to feed the system (Fig. 5), the NO oxidation reaction is slightly faster than the NO_2 degradation. However, when the relative humidity is high, then the photocatalytic reaction rates are slower and NO_2 is produced in the system, most likely because the photocatalytic oxidation of NO produces NO_2 as intermediate (Eqs. (8) and (9)).

It is also possible to compare experiments applying different NO/NO_2 concentration ratios employing a photocatalytic sample and also a non-active stone (Fig. 6). When NO_2 is high (e.g. $C_{NO_2} = 0.5$ ppm) it is possible to observe NO_2 degradation, even without a photocatalytic active surface, because of the NO_2 photolysis under UV light (Eq. (12)). In addition, as discussed above, when only NO is fed to the reactor and a photocatalytic stone is used, NO_2 appears in the system. However, when a normal stone is applied, NO_2 is not formed indicating again that it is an intermediate of the photocatalytic reactions (Eq. (9)).

Finally, an overview of the effect of relative humidity and irradiance over the NO and NO_2 degradation is shown in Fig. 7. The tendency is identical to Figs. 3–5 (increment of conversion with increment of irradiance and decrement of relative humidity), except for the NO_2 conversion when the relative humidity changes to higher values. In this case, due to the lower photocatalytic reaction rate, as explained before, NO_2 is produced in the system, especially for higher values of irradiance. This is probably because under high irradiance the oxidation of NO to NO_2 is still fast and NO_2 is accumulated. On the other hand, when the irradiance is low, the NO oxidation rate decreases and less NO_2 is produced.

5. Conclusions

In the present work, NO and NO_2 photocatalytic and homogeneous reactions are experimentally studied employing a photocatalytic concrete stone and a normal non-active concrete. Different experiments were carried out employing a continuous photoreactor applying NO and NO_2 as the target pollutants. Different operating conditions were selected to perform the experiments (varying NO and NO_2 inlet concentration, relative humidity and irradiance respectively). The following conclusions can be drawn:

- Homogeneous reactions are observed when NO_2 is fed to the photoreactor under UV light.
- NO_2 is detected as an intermediate in the photocatalytic process, especially when the reaction is not fast (e.g. when RH = 70%) or when NO_2 is not fed to the system. In these cases, NO_2 is produced in the photoreactor during the NO photocatalytic oxidation, and then NO_2 cannot be completely converted to nitrates.
- NO is formed in the system, even in the presence of a photocatalytic sample, when only NO_2 is fed at high concentration or at

high relative humidity, because the homogeneous photolysis of NO_2 becomes dominant.

- For the other employed operating conditions, a successful NO and NO_2 degradation was observed applying a photocatalytic concrete stone containing TiO_2.

This paper contributes to understand different national and international standards for the assessment of photocatalytic materials, where in some of them, both NO and NO_2 are employed as the target pollutants. In addition, this research also helps to a better comprehension of the mechanism that governs the NO_x reduction in a photocatalytic street with $DeNO_x$ concrete stones. Nitrogen oxides are not just reactants for the photocatalytic oxidation, but also they can interact in a complex way with other components present in the atmosphere.

From these experimental data, an intrinsic kinetic model for the NO_x degradation, including heterogeneous as well as homogeneous reactions, is foreseen. With such kinetic model, the simulation of NO_x concentration distribution in a $DeNO_x$ street can be developed.

Acknowledgements

The authors wish to express their gratitude to the following sponsors of the research group: Bouwdienst Rijkswaterstaat, Graniet-Import Benelux, Kijlstra Betonmortel, Struyk Verwo, Insulinde, Enci, Provincie Overijssel, Rijkswaterstaat Directie Zeeland, A&G Maasvlakte, BTE, Alvon Bouwsystemen, V.d. Bosch Beton, Selor, Twee “R” Recyling, GMB, Schenk Concrete Consultancy, De Mobiele Fabriek, Creative Match, Intron, Geochem Research, and Icopal (chronological order of joining), and their further thankfulness to the European Commission (I-SSB Project, Proposal No. 026661-2). In addition, the authors would like to thank the help of M. Hunger, G. Hüsken, H.T.J. Overman, and P.H. Cappon.

References

[1] EU – The Council of the European Union, Council Directive 1999/30/EC – Relating to Limit Values for Sulphur Dioxide, Nitrogen Dioxide and Oxides of Nitrogen, Particulate Matter and Lead in Ambient Air, 1999.
[2] Traffic Emissions Policy Document, VROM, The Netherlands. Internet: http://www.sharedspaces.nl/docs/internationaal/VerkeersemENG.pdf.
[3] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis Fundaments and Applications, BKC, Inc., Chiyoda-ku, Tokyo, 1999.
[4] G. Hüsken, M. Hunger, H.J.H. Brouwers, Experimental study of photocatalytic concrete products for air purification, Build. Environ. 44 (2009) 2463–2474.
[5] G.L. Guerrini, E. Peccati, Photocatalytic cementitious roads for depollution, in: International RILEM Symposium on Photocatalysis, Environment and Construction Materials, Florence, Italy, 2007.
[6] ISO 22197-1, Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test Method for Air Purification Performance of Semiconducting Photocatalytic Materials – Part 1: Removal of Nitric Oxide, first edition, 2007.
[7] UNI 11247, Determinazione dell’Attività di Degradazione di Ossidi de Azoto in Aria da Parte de Materiali Inorganici Fotocatalitici, Italian Standard, 2007.
[8] XP B44-011, Méthode d’essai pour l’évaluation des matériaux photocatalytiques vis-à-vis de la dégradation des NO_x. Méthode à un seul passage en mode tangentiel, French Standard, 2009.
[9] S. Marsili-Libelli, Simplified kinetics of tropospheric ozone, Ecol. Mod. 84 (1996) 233–244.
[10] B.N. Shelimov, N.N. Tolkachev, O.P. Tkachenko, G.N. Baeva, K.V. Klementiev, A.Y. Stakheev, V.B. Kazansky, Enhancement effect of TiO_2 dispersion over alumina on the photocatalytic removal of NO_x admixtures from O_2–N_2 flow, J. Photochem. Photobiol. A: Chem. 195 (2008) 81–88.
[11] S. Devahasdin, C. Fan, J.K. Li, D.H. Chen, TiO_2 photocatalytic oxidation of nitric oxide: transient behavior and reaction kinetics, J. Photochem. Photobiol. A: Chem. 156 (2003) 161–170.
[12] H. Wang, Z. Wu, W. Zhao, B. Guan, Photocatalytic oxidation of nitrogen oxides using TiO_2 loading on woven glass fabric, Chemosphere 66 (2007) 185–190.
[13] M.M. Ballari, M. Hunger, G. Hüsken, H.J.H. Brouwers, NO_x photocatalytic degradation employing concrete pavement with titanium dioxide, Appl. Catal. B: Environ. 95 (2010) 245–254.