INFLUENCE OF PARAMETERS ON THE PHOTOCATALYTIC OXIDATION OF NITRIC OXIDE AT THE SURFACE OF TITANIUM DIOXIDE-MODIFIED CONCRETE MATERIALS

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INTRODUCTION

Titanium dioxide (TiO_2) is a well-known photocatalyist leading to the transformation of nitrogen oxides (NO/NO_2) under UV irradiation, via catalytic heterogeneous reactions, to nitric acid (HNO_3), which remains on the TiO_2 surface and can we wash out by rain or other washing processes. A great variety of photocatalytic products, aimed to eliminate the nitrogen oxides from the atmosphere are offered by the market. Nevertheless, their anti-polluting ability in outdoor conditions remains an open question.

The work presented here forms part of a series of systematic studies, carried out within the framework of the LIFE $MINO_x$-STREET European project, co-financed by the EU, whose primary objective has been to evaluate the performance of a wide variety of commercial photocatalytic materials and select several among them promising to be implemented at urban scenarios. To do that, rigorous essays and tests on their physical-chemical properties and expected photocatalytic efficiency, not only under controlled laboratory conditions but also in real atmosphere, have been done and three different photocatalytic materials considered for their application on concrete pavements at real scale have been selected for further investigation. More concretely, the influence of several key environmental parameters on their air-purifying capacity, within a range of relevant atmospheric conditions, has been studied and it is presented here.

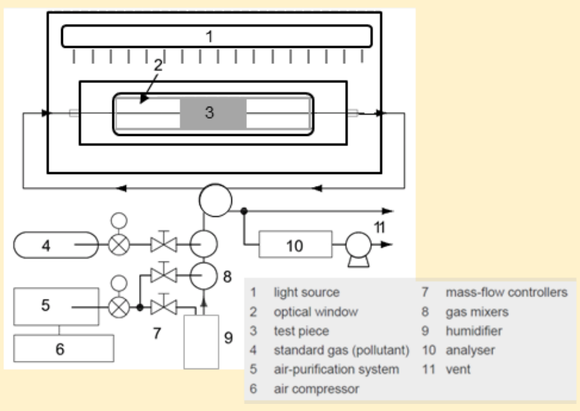
Further, a first-order rate approximation has been followed to compute analogue surface deposition velocities that can be used in resistance models to estimate deposition flows on photocatalytic surfaces.

EXPERIMENTAL AND KINETIC APPROXIMATION

The photocatalytic activity of three promising photocatalytic concrete been essayed under the ISO international standard 22197-1:2007 [1].

Water emulsion on bituminous concrete pavement

Water emulsion and photocatalytic coating on sidewalk concrete pavement



Scheme of the ISO 22197-1 test equipment used to test concrete samples

In the standard ISO experiment , test gas mixture flow (NO, air, H_2O) (50% relative humidity) is passed over the flat rectangular sample of typically 99 mm x 49 mm x 5 mm, placed inside a bed flow photo-reactor, and is irradiated by UV-A light (10 W m^{-2}) through a UV transparent window with a distance to the sample of 5 mm. Under the conditions applied, a laminar-plugged flow is assumed and very short reaction times of only a few seconds are obtained. During the essays, NO inlet and outlet concentrations are analyzed and registered.

Test conditions were varied for the different parameters under study: with NO inlet concentration in 100 to 1000 ppb range, UV-A irradiance intensity in 2 to 40 W m^{-2} range, relative humidity in the extended range from 20 to 85 % and flow rate fixed at 3 or 1.5 l min^{-1}.

Summary of test conditions

Operating conditions	Value
Flow rate (l min^{-1})	1.5 and 3.0
Flow velocity above reactive surface (m s^{-1})	0.1 and 0.2
Temperature (°C)	20 °C
Pressure (kPa)	101.325
NO inlet concentration (ppbv)	250, 500, 750 and 1000
Relative humidity (%)	20, 35, 50, 65, 75 and 85
Reactive surface (mm x mm)	49 x 99
Irradiance (300-400 nm) (W m^{-2})	2, 5, 10, 20 and 40

REFERENCES

[1] International standard ISO 22197-1:2007, Geneve, 2007.
[2] B. J. Finlayson-Pitts, L. M. Wingen, A. L. Sumner, D. Syomin and K. A. Ramazan. *Phys. Chem. Chem. Phys.*, **5**, (2003) p. 223-242.
[3] S. Devahasdin, C. Fan, K. Li and D. H. Chen., *J. Photoch. Photobio. A*, **156**, (2003) p.161-170.
[4] W. A. Jacoby, D. M. Blake, R. D. Noble, C. A. Kovel, *J. Catal.*, (1995), 157 p. 87-96.
[5] T. H. Lim, S. M. Jeong, S. D. Kim and J. Gyenis., *J. Photoch. Photobio. A*, **134** (3), (2000) p. 209-17.
[6] G. Husken, M. Hunger and H. Brouwers, *Build. Environ.*, **44**, (2009) p. 2463-74.

FIRST-ORDER KINETIC APPROXIMATION

Assuming NO photocatalytic decomposition follows a first order kinetics under relevant atmospheric conditions, a first-order rate coefficient (k_r, s^{-1}), can be determined from the experimental data obtained:

$$k_r = -\frac{ln(C_{out}-C_{in})}{t_r} \quad (1)$$

where C_{in} and C_{out} are NO concentration at the inlet and exit of the photo-reactor (ppbv) and t_r is the reaction time of the gas-phase N. The dimensionless reactive uptake coefficient, γ, has been introduced in heterogeneous chemistry [2], independent on the geometry of the reactor, as:

$$\gamma = \frac{4 \cdot k_r}{\bar{\upsilon} \cdot S/V} \quad (2)$$

considering that $\bar{\upsilon}$ is the mean molecular velocity of the gas NO (m s^{-1}) defined by the kinetic gas theory:

$$\bar{\upsilon} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad (3)$$

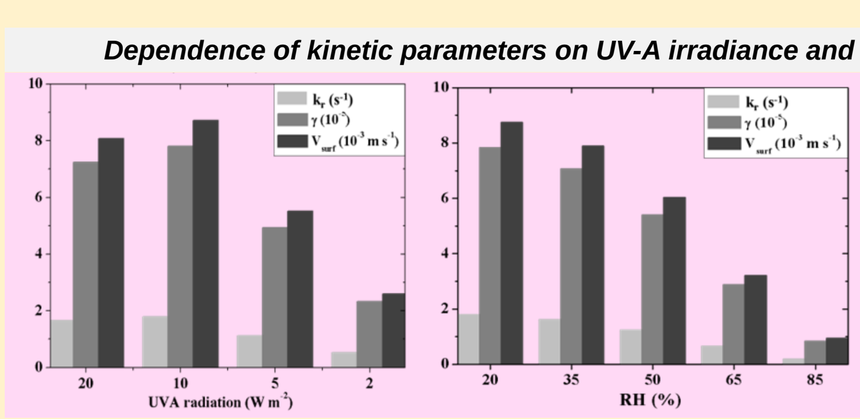
where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K) and M is the molecular mas of NO (kg mol^{-1}). Then, an analogue surface deposition velocity can be defined:

$$V_{surf} = \frac{\gamma \cdot \bar{\upsilon}}{4} \quad (4)$$

In this way, NO uptake coefficients (γ) and surface deposition velocities (V_{surf}) have been estimated from the experimental data.

RESULTS AND DISCUSSION

Dependence of kinetic parameters on UV-A irradiance and relative humidity

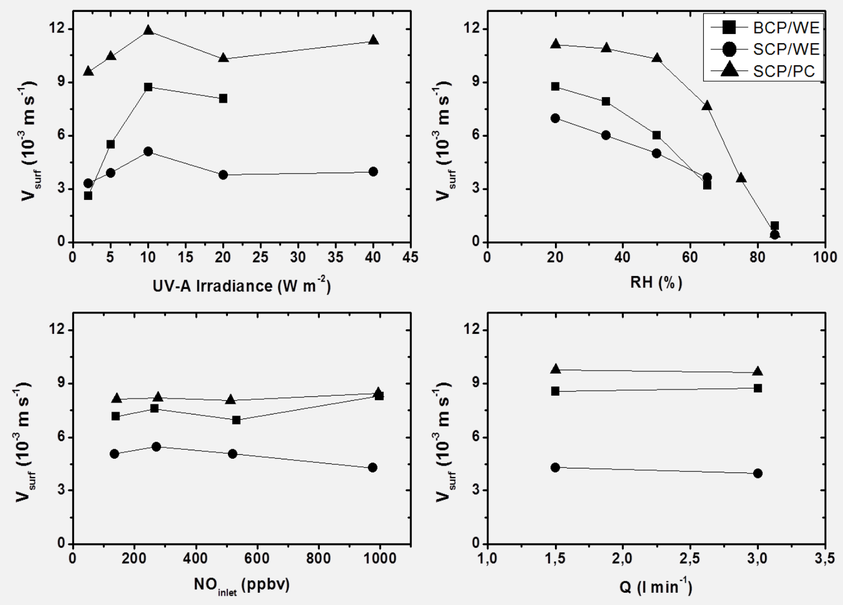


	Irradiance (W m^{-2})		Relative Humidity (%)		NO inlet concentration (ppbv)		Flow rate (l min^{-1})	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
BCP/WE	5.58	2.49	4.81	2.92	6.72	0.53	7.76	0.11
SCP/WE	3.61	0.68	3.95	2.28	4.44	0.39	3.70	0.20
SCP/PC	9.58	0.81	6.57	3.94	7.36	0.13	8.69	0.07

Kinetic parameters are independient on the flow rate. On the other hand, the dependence of k_r on NO inlet concentration did not show a clear trend for any of the essayed materials, as it was expected by following the used numerical scheme (see table).

NO degradation rate increases with the light intensity in the activation region of the spectrum [3]. All tested materials exhibited two different regimes: a first-order regime where electron-hole pairs are consumed rapidly by chemical reactions and a half-order regime, above 10-20 W m^{-2}, where the recombination rate is dominant which decrease the photocatalytic reaction rate, according to other studies [4, 5]. The results from the experiments also showed a negative dependence of the NO removal capacity on relative humidity in the whole range studied [6].

Average V_{surf} (10^{-3}) (m s^{-1}) obtained from experimental data



The test conditions used in the work have covered the range of typical atmospheric conditions found under nitrogen oxides pollution episodes. A UV-A light intensity lower than 10 W m^{-2} or relative humidity values above 20-40% have, as a result, a significant drop in the photocatalytic activity of all materials tested.

CONCLUSIONS

The standard test method ISO 22197-1: 2007, has been successfully applied to determine the NO photocatalytic activity of three different types of photocatalytic products, designed to be applied on both bituminous and sidewalk concrete pavements. Moreover, the influence of several key parameters (as UV-A irradiance, relative humidity, NO inlet concentration and flow rate) on the NO removal capacity has been investigated.

In addition, a first-order kinetics approximation is proposed to estimate kinetic parameters (as uptake coefficient or analogue surface deposition velocities) independent of the experimental photo-reactor configuration and the studied concentration levels, allowing a previous evaluation of the potential NO removal capacity of the photocatalytic materials tested under realistic weather conditions.

The nature of photocatalytic products and substrate on which they are applied determine the NO remediation activity measured and, consequently, the first-order rate constants, uptake coefficients and analogue surface deposition velocities estimated.

The amount of NO removed from the gas phase by photocatalytic oxidation is strongly affected by changes of the light intensity as well as of the relative humidity.

Acknowledgements: With the contribution of LIFE financial instrument of the EU.