Appendix
The NO removal ISO Standard[1,2]

Introduction

The key photocatalytic reactions associated with the reduction of ambient NO_x levels using a TiO_2-based photocatalyst, [3-6], i.e.

$$4NO + O_2 + 2H_2O \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4HNO_2 \qquad (1)$$

$$4HNO_2 + O_2 \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4NO_2 + 2H_2O \qquad (2)$$

$$2H_2O + 4NO_2 + O_2 \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4HNO_3 \qquad (3)$$

Thus, in the photocatalytic reactions (1) and (2), the NO component of NO_x is oxidised to NO_2, *via* the intermediate formation of nitrous acid, HNO_2, and then the existing and photocatalyst-generated NO_2 is oxidised to nitric acid, *via* reaction (3). There is, however, a well-known problem [2,7-11] with this system, in that as the final product, HNO_3, accumulates on the surface of the TiO_2 photocatalyst, the following photocatalysed reaction becomes increasingly important,

$$2HNO_3 + NO \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 3NO_2 + H_2O \qquad (4)$$

As a consequence, all TiO_2-based photocatalysts for NO_x removal eventually accumulate sufficient surface HNO_3 so that they only function to promote the oxidation of NO to NO_2 [8,2], i.e.

$$2NO + O_2 \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 2NO_2 \qquad (5)$$

The problem of HNO_3 accumulation is usually addressed in commercial photocatalytic paints and concrete by including in the formula an acid scavenger, such as $CaCO_3$ [12] or NaOH [2], since, in contrast to HNO_3, the accumulation of a nitrate salt does not appear to promote reaction (5). Photocatalyst coatings, such as glass, tiles or plastics, that do not have an effective, acid-removing additive, must therefore, rely on the regular removal of the surface accumulated HNO_3 by surface water, such as rain, which is clearly an issue for indoor products and external-use products where regular rainfall is unlikely [2]. As a consequence, the latter materials are usually promoted for their ability to destroy volatile or non-volatile organic pollutants, rather than their NO_x removal capacity

The ISO photocatalytic reactor

The ISO standard employs an inert flat-bed photoreactor system (Fig. 1) designed to hold a 5 × 10 cm^2 test sample under illumination with UVA light (irradiance = 1 mW cm^{-2}). Humidified (RH = 50% at 25 °C) air and dry NO, mixed to give a NO concentration of 1.0 ppmv, are passed into the system at 3.0 dm^3 min^{-1} *via* mass flow rate controllers. The gas mixture is made to pass through a narrow gap of 5 mm between the top glass window and the test sample below, and the outlet gas stream from the reactor is sampled through a valve attached to a suitable NO_x detection system, usually based on chemiluminescene. The concentration of NO and NO_2 in the outlet stream is monitored for ca. 30 min before the light is switched on, during the 5 h irradiation period of the test, and for 30 min after the light has been switched off. A schematic illustration of a typical set of results, i.e. plots of [NO] and [NO_2] vs time recorded before, during and after UV irradiation are illustrated in Fig. 2. The test sample's overall ability to photocatalytically remove NO_x, $n(NO_x)_{rem}$ was calculated from the difference between the total NO removed, $n(NO)_{rem}$, and NO_2 generated $n(NO_2)_{gen}$ during the irradiation period [12].

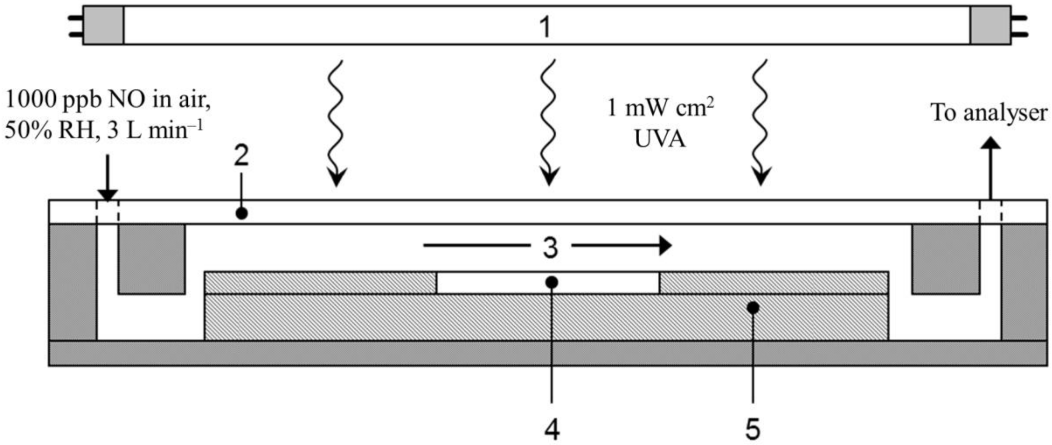


Fig. 1 Cross-sectional schematic of the photoreactor used in the NO air-purification ISO method: (1) UV light source, (2) glass cover, (3) test gas flow, (4) flat test sample, (5) height-adjusting plate.

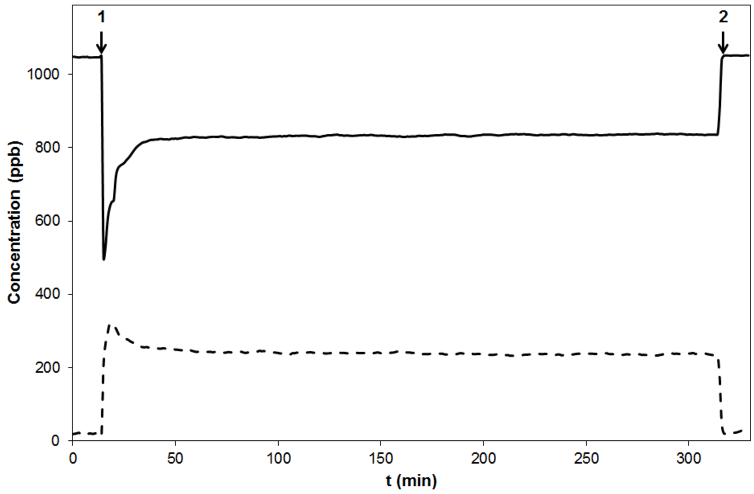
Thus, in every NO ISO test run, the recorded [NO] and [NO_2] vs time profiles, such as that illustrated in Fig. 2 were used to calculate the amounts of NO removed, NO_2 generated and NO_x removed as a proportion of the total amount of NO that flowed through the system over the 5 h of irradiation period. In this work the key calculations were based on the following equations,

$$\%NO(rem) = \int_{t_0}^{t_{end}} \frac{[NO]_{in} - [NO]_{exit}}{[NO]_{in}}\, dt \times 100\% \quad (6)$$

$$\%NO_2(gen) = \int_{t_0}^{t_{end}} \frac{[NO_2]_{exit}}{[NO]_{in}}\, dt \times 100\% \quad (7)$$

$$\%NO_x(rem) = \int_{t_0}^{t_{end}} \frac{[NO]_{in} - [NO]_{exit} + [NO_2]_{exit}}{[NO]_{in}}\, dt \times 100\% \quad (8)$$

where, %NO(rem), $\%NO_2$(gen) and $\%NO_x$(rem), are the percentages of NO removed, NO_2 generated and NO_x removed, respectively. It follows from eqns (6) to (8) that $\%NO_x$(rem) = %NO(rem) - $\%NO_2$(gen). The parameters, $[NO]_{in}$ and $[NO]_{exit}$ are the measured concentrations, in ppbv (or ppm), of NO, in the gas stream on entry and exit of the photoreactor, respectively, at any time, *t*, during the irradiation period. The parameter $[NO_2]_{exit}$ is the exit concentration of NO_2, measured at the same time, *t*, as $[NO]_{exit}$. The integrations described by eqns (6) – (8), cover the irradiation period of interest, which is usually between t_o = 0 min to t_{end} = 300 min, which mark the points at which the UV light is switched on and then off, respectively, during a typical run,



see Fig. 2. The values of %NO(rem), $\%NO_2$(gen) and $\%NO_x$(rem) calculated for this period are average values and referred to as such.

Fig. 2 Typical data set generated, i.e. NO removed (solid line) and NO_2 generated (broken line), during an NO ISO standard test (inlet [NO] = 1000 ppb), with key time points, namely, (1) when UV light is switched on, i.e. when t_o (in eqns (6)-(8) in main text) = 0 min and (2) when UV light is switched off, i.e. when t_{end} = 300 min.

A typical report sheet provided by IPS for a photocatalytic film is illustrated in Fig. 3, which includes reaction details and calculated values of %NO(rem), $\%NO_2$(gen) and $\%NO_x$(rem).

Additional notes

(i) UV Pre-conditioning

In accordance with the standard NO ISO, [1], all samples are pre-irradiated for 16 h with UV light (1 mW cm^{-2}) to decompose any residual organic matter. If customers require a longer pre-irradiation time, this must be requested in advance and will incur an additional charge..

(ii) The Sensitive and Super-Sensitive tests

In accordance with the standard NO ISO, [1], samples which might exhibit a lower performance can be run under the following alternative sensitive test conditions, namely: a flow rate of 1.5 L min^{-1} and with two samples (10x5 cm^2) in series. This improves the sensitivity of the system by 4. IPS have also developed a Super-sensitive test in which a flow rate of 0.25 L min^{-1} and with three samples (10x5 cm^2) in series are use. This improves the sensitivity of the system (compared to the standard test conditions) by 36 [13].

IPS
INTERNATIONAL PHOTOCATALYST STANDARDS TESTING CENTRE

Fine ceramics - Test method for air-purification performance of semiconducting photocatalytic materials

BS ISO 22197-1:2007
ISO 22197-1:2007 (E)

Removal of nitric oxide

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Customer Name:	IPS
Customer contact:	IPS
Sample name:	P25 Standard
Sample description:	P25 on glass

Testing conditions

Date (dd/mm/yyyy)=	12/04/2018
T (°C) =	20.9
RH (%) =	51
STP flow (L/min) =	2.70
irradiance (mW/cm²) =	1
NO supply conc. (ppm) =	0.97
Sample Area (cm)	5x10

Results	Amount (µmol)	Area (%)
(i) NO supplied to the reactor	35.37	100.00
(ii) NO removed by the test piece	9.46	26.73
(iii) total NO unreacted	25.92	73.27
(iv) amount of NO_2 generated by the test piece	7.85	22.18
(v) net amount of NO_x removed by the test piece = ((ii)-(iv))	**1.61**	4.55

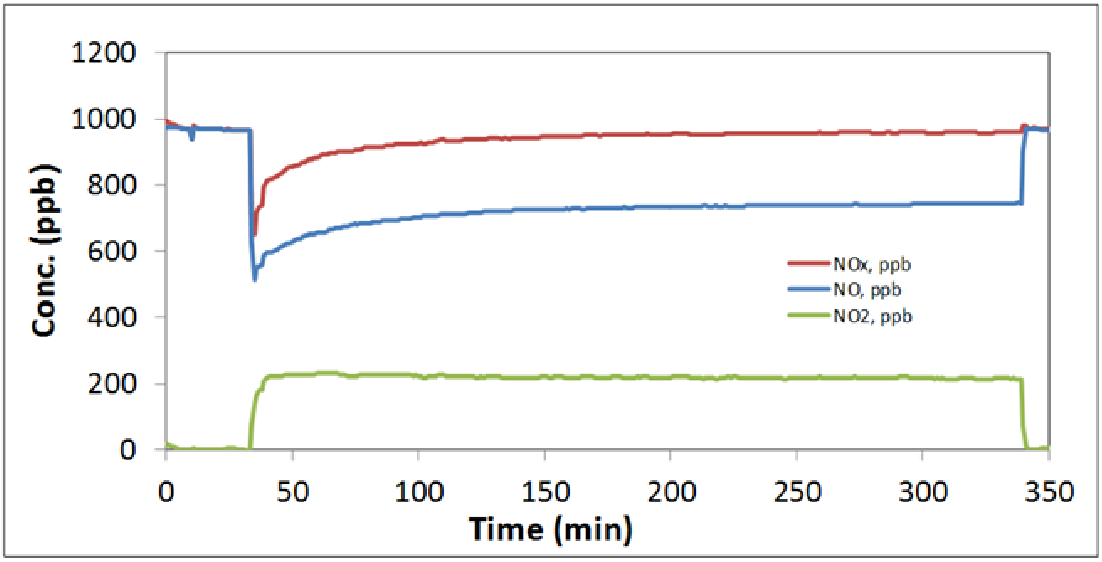

Figure : Trace of $NO/NO_x/NO_2$ concentration during the ISO test for tested sample.

Fig. 3: IPS report sheet for a typical TiO_2 powder film

References

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