



# Influence of inlet concentration and light intensity on the photocatalytic oxidation of nitrogen(II) oxide at the surface of Aeroxide<sup>®</sup> TiO<sub>2</sub> P25

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## ABSTRACT

Air pollution by nitrogen oxides represents a serious environmental problem in urban areas where numerous sources of these pollutants are concentrated. One approach to reduce the concentration of these air pollutants is the light-induced oxidation in the presence of molecular oxygen and a photocatalytically active building material, e.g., paints, roof tiles, or pavement stones. Herein, results of an investigation concerning the photocatalytic oxidation of nitrogen(II) oxide (NO) in the presence of molecular oxygen and UV(A) irradiated TiO<sub>2</sub> powder are presented.

The standard operating procedure described in ISO 22197-1 which was developed to characterize the photocatalytic activity of air-cleaning products was successfully applied to determine the photocatalytic activity of a bare TiO<sub>2</sub> powder. The experimental data reveal that at the light intensity stipulated by the operation procedure the amount of NO removed from the gas phase by photocatalytic oxidation is strongly affected by small changes of this light intensity as well as of the NO concentration in the gas stream in the photoreactor. Therefore, these parameters have to be controlled very carefully. Based upon the experimental data obtained in this study a rate law for the photocatalytic NO oxidation inside the photoreactor is derived.

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## 1. Introduction

Air pollution by nitrogen oxides (mainly NO and NO<sub>2</sub>) presents a serious environmental problem in urban areas where numerous sources of these pollutants are concentrated [1]. Forced by rigorous laws that have been approved to protect the environment by establishing limiting values for the concentrations of the most frequent air pollutants, severe efforts have been made to develop methods to reduce both the concentration of NO and of NO<sub>2</sub> [2].

One approach to reduce the concentration of air pollutants is the light-induced oxidation in the presence of a photocatalytically active material and molecular oxygen. Titanium dioxide (TiO<sub>2</sub>) in its anatase form is well known as a powerful photocatalyst applicable to mineralize various organic and inorganic compounds [3–6]. It has been shown that nitrogen oxides can be easily oxidized under irradiation with UV(A) light in the presence of titanium dioxide and molecular oxygen [7–19] yielding HNO<sub>3</sub> as the final oxidation product. Since some years photocatalytically active building materials, e.g., paints, roof tiles, pavement stones and other concrete based

products, are available and intense work was performed to clarify the reaction pathways of the photocatalytic transformation of nitrogen oxides and to obtain an insight into the respective kinetics [20–34]. To assess the photocatalytic oxidation efficiency of the air-cleaning products a standard operation procedure was developed and published by ISO in 2007 [35]. For this standard test procedure nitrogen(II) oxide (NO) is employed as the probe molecule. An NO inlet concentration of 1 ppm, a light intensity of 10 W m<sup>-2</sup>, a relative humidity of 50%, a temperature of 25 °C, and a reactive surface area of 50 cm<sup>2</sup> are stipulated by this activity assessment procedure [35].

To the best of our knowledge, all photocatalytically active building materials available on the market contain titanium dioxide powder as the photocatalyst. Therefore, an investigation concerning the suitability of the ISO standard test procedure [35] for the assessment of the photocatalytic efficiency of photocatalyst powders themselves appeared to be timely. Moreover, the robustness of the results regarding variation of the key process parameters, i.e., the NO inlet concentration and the light intensity, has been investigated here. An unforeseen outcome of this work was the derivation of a rate law for the photocatalytic NO oxidation, which, to the best of our knowledge, is presented here for the first time for the kinetic description of a heterogeneous photocatalytic reaction of an air pollutant.

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## Nomenclature

$A$	photocatalytically active, geometric surface area of the sample ( $\text{m}^2$ )
$c$	concentration ( $\text{ppm}$ or $\text{mol m}^{-3}$ )
$c_{\text{NO}}^m$	mean NO concentration inside the photoreactor during UV(A) irradiation ( $\text{mol m}^{-3}$ )
$h_r$	relative humidity (%)
$h_a$	absolute humidity ( $\text{g m}^{-3}$ )
$I$	photon flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$K, K(I)$	adsorption constant ( $\text{m}^3 \text{mol}^{-1}$ )
$k, k(I)$	rate constant ( $\text{mol m}^{-2} \text{s}^{-1}$ or $\text{m s}^{-1}$ )
$n$	amount (mol)
$p$	pressure (Pa)
$R$	gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$r$	rate ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$r_{r,\text{NO}}$	average reaction rate of NO ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$T$	temperature (K)
$t$	time (s)
$\Delta t_{\text{irr}}$	irradiation time (s)
$\dot{V}$	volume flow ( $\text{m}^3 \text{s}^{-1}$ or $\text{L min}^{-1}$ )
$\eta$	set of parameters describing the charge carrier recombination in the photocatalyst, the adsorption of water and molecular oxygen at the photocatalyst surface, the interfacial electron transfer, and the light absorbing properties of the photocatalyst coverage
$\Theta$	

### Subscripts

<i>air</i>	air
<i>ads</i>	adsorption
<i>deg</i>	degraded
<i>des</i>	desorption
<i>in</i>	inlet conditions
<i>out</i>	outlet conditions
<i>Ox</i>	oxidizing species
<i>r</i>	reaction
<i>rem</i>	removed

## 2. Experimental details

### 2.1. Sample preparation

The photocatalyst Evonik-Degussa Aeroxide® TiO<sub>2</sub> P25 ( $0.85 \pm 0.02 \text{ g}$ ) was placed into a rectangular plexiglass folder (height 0.2 cm, width 9.2 cm, length 4.3 cm), covered with a polished plexiglass plunger, and pressed with a bearing pressure of  $1080 \text{ kg m}^{-2}$  for 1 min. The resulting briquettes with a surface area of  $39.6 \text{ cm}^2$  were irradiated for three days with a UV(A)-lamp (Philips, Cleo Performance UV type 3,  $\lambda_{\text{max}} = 355 \text{ nm}$ , 100 W) at a light intensity of  $10 \text{ W m}^{-2}$  to remove all organic contaminants possibly adsorbed on their surfaces.

### 2.2. Photocatalytic NO oxidation

The photocatalytic oxidation of NO was accomplished according to ISO 22197-1 [35]. The test equipment enables the determination of the pollutant removal capabilities of a photocatalytically active material by supplying the test gas continuously, while providing UV(A) irradiation to activate the photocatalyst. It consists of a test gas supply (NO), a photoreactor (PMMA, borosilicate glass) built closely following the original concept of the JIS [36], a light source (Philips, Cleo Compact,  $\lambda_{\text{max}} = 355 \text{ nm}$ , 15 W), and a pollutant analyser (NO<sub>x</sub>-Analyser, Horiba, APNA 360) (Fig. 1). The

NO<sub>x</sub> analyser determines the volume concentrations of NO, NO<sub>2</sub>, and the sum of these, NO<sub>x</sub>, by chemiluminescence analysis. The standard conditions employed were an inlet volume concentration of 1 ppm NO and a relative humidity  $h_r = 50\%$  (equivalent to  $h_a = 11.7 \text{ g m}^{-3}$ ) at a temperature of 25 °C. For a single degradation test the sample was placed into the photoreactor and covered with an UV(A) transparent glass. At the beginning of each individual test run the pollutant volume concentration (1 ppm equivalent to  $41 \mu\text{mol m}^{-3}$ ) was adjusted via a bypass mode, without photoirradiation. Therefore, an air flow of  $3.0 \text{ L min}^{-1}$  was combined in a mixing chamber with the needed NO flow of  $6.1 \cdot 10^{-2} \text{ L min}^{-1}$  (Linde, 50 ppm NO in N<sub>2</sub>) employing mass flow controllers (Brooks Instrument). Having established the constant volume concentration of 1 ppm a dark adsorption of the pollutant on the catalyst surface was accomplished by switching from bypass into reactor mode. After the pollutant volume concentration rose up to 1 ppm again the photoirradiation was performed for 2 h. At the end of the degradation reaction the lamp and the NO-flow were switched off simultaneously. The NO concentration was continuously monitored until it had decreased to 0 ppm.

Subsequently, the inlet volume concentration of NO was adjusted within a range from 0.05 to 1.3 ppm ( $c_{\text{NO},\text{in}} = 2\text{--}53 \mu\text{mol m}^{-3}$ ) by varying the NO flow from  $3.0 \cdot 10^{-3}$  to  $8.0 \cdot 10^{-2} \text{ L min}^{-1}$  while the air flow remained constant at a value of  $3.0 \text{ L min}^{-1}$ .

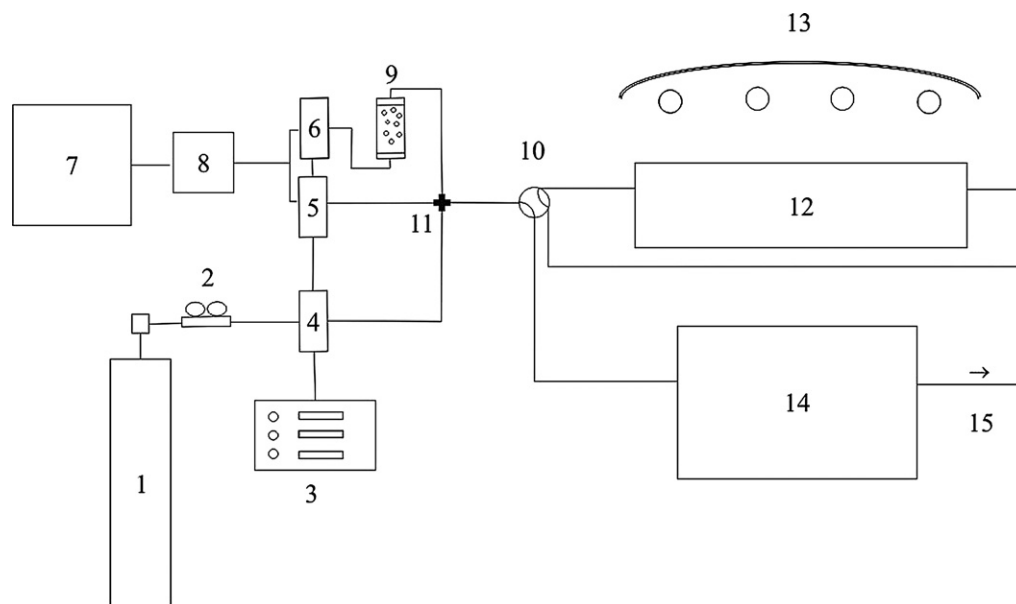
Moreover, the light intensity was varied from 0 to  $15 \text{ W m}^{-2}$  ( $I = 0\text{--}44.8 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) by changing the distance between the UV(A)-lamp and the photoreactor. The light intensity was directly measured before and after the degradation test at three different positions in the photoreactor exactly at the height of the surface of the photocatalyst layer using a radiometer (UV(A)-365, Lutron Electronic) equipped with a sensor collecting the UV(A) irradiation in a range from 320 to 390 nm with a sensibility maximum at 365 nm.

The absolute humidity was calculated from the measurement of the relative humidity and the temperature with a hygrometer (ELV Elektronik AG, TFM 100), which was placed inside the photoreactor. The humidity remained constant at standard conditions ( $11.7 \text{ g m}^{-3}$  at 25 °C) in all experimental runs.

## 3. Results and discussion

The photocatalytic degradation of NO on Aeroxide® TiO<sub>2</sub> P25 briquettes was studied varying the inlet concentration of NO ( $2\text{--}53 \mu\text{mol m}^{-3}$ ) and the incident light intensity ( $0\text{--}15 \text{ W m}^{-2}$ ,  $0\text{--}44.8 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ). In the absence of UV(A) light  $c_{\text{NO},\text{out}} = c_{\text{NO},\text{in}}$  was found in the presence as well as in the absence of the photocatalyst, clearly indicating that no dark reactions occur. Under all investigated experimental conditions a decrease of the NO gas phase concentration was observed under UV(A) irradiation in the presence of the TiO<sub>2</sub> briquettes while within the limits of experimental error no reduction of the NO concentration by homogeneous photoreaction(s) was observed during UV(A) irradiation in the absence of the photocatalyst. The change of the NO concentration at the reactor outlet during a typical experimental run under UV(A) illumination is shown in Fig. 2.

The NO concentration was adjusted to the desired inlet concentration (in Fig. 2:  $c_{\text{NO},\text{in}} = 1 \text{ ppm} = 41 \mu\text{mol m}^{-3}$ ) in a bypass mode. When this value was found to be stable the reaction was started by switching the system into the reactor mode without UV(A) irradiation. Immediately thereafter, the NO concentration at the reactor outlet was found to decrease, subsequently approaching again the initial inlet concentration (1 ppm). This behaviour can be explained by the dark adsorption of NO followed by the saturation of the surface of the photocatalyst sample and the exposed surface area of the photoreactor with adsorbed NO. After the NO concentration



**Fig. 1.** Experimental set-up (here shown in the bypass mode): (1) NO supply, (2) pressure reducing valve, (3) control for (4–6) mass flow controllers, (7 and 8) air supply, (9) humidifier, (10) four-way valve, (11) mixing chamber, (12) photoreactor, (13) light source, (14) NO analyzer, and (15) exhaust gas.

was found to be stable for at least 5 min, the UV(A) light source was switched on to start the photocatalytic reactions. An immediate decrease of the NO concentration was observed. Following 2 h of irradiation with UV(A) light, the light-source was switched off and the supply of the NO gas was closed. The NO concentration was subsequently recorded until  $c_{\text{NO}} = 0$  ppm to allow the calculation of the amount of NO desorbing from all surfaces inside the reactor after switching off the UV(A) light source and the inlet flow of NO gas.

According to ISO 22197-1 [35] the total amount of the removed NO ( $n_{\text{rem}}$ ) was calculated using the equation

$$n_{\text{rem}} = n_{\text{ads}} + n_{\text{deg}} - n_{\text{des}} \quad (1)$$

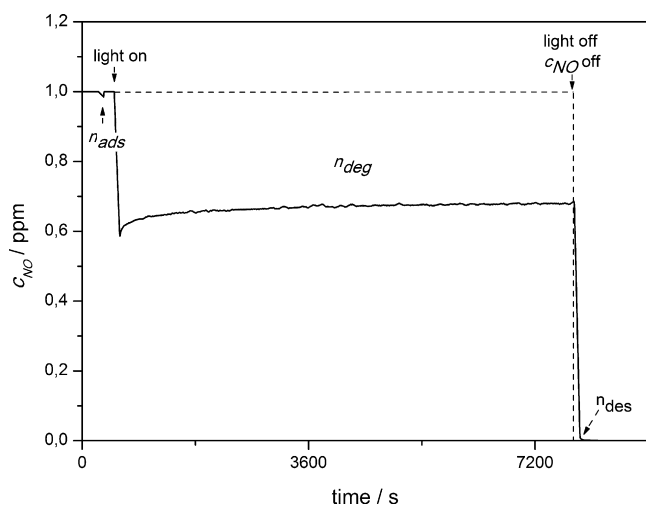
The adsorbed ( $n_{\text{ads}}$ ), degraded ( $n_{\text{deg}}$ ) and desorbed ( $n_{\text{des}}$ ) amounts of NO were calculated by using Eqs. (2)–(4):

$$n_{\text{ads}} = \frac{p(\dot{V}_{\text{air}} + \dot{V}_{\text{NO}})}{RT} \cdot \sum_{t_{\text{R}}}^{t_{0,\text{hv}}} (c_{\text{NO},\text{in}} - c_{\text{NO},\text{out}}) \cdot \Delta t \quad (2)$$

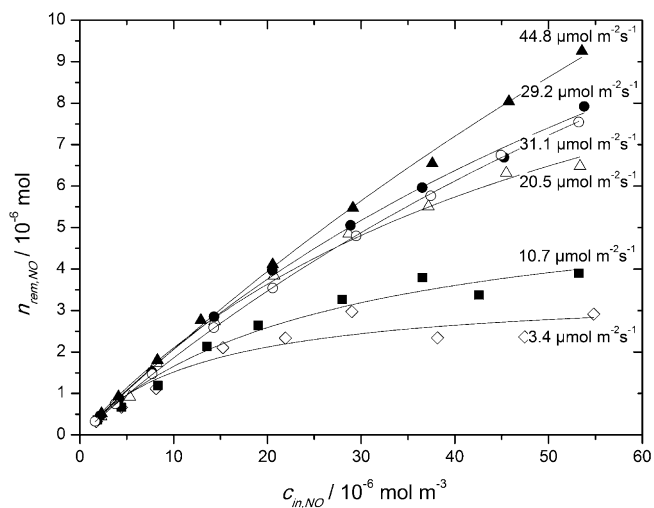
$$n_{\text{deg}} = \frac{p(\dot{V}_{\text{air}} + \dot{V}_{\text{NO}})}{RT} \cdot \sum_{t_{0,\text{hv}}}^{t_{\text{E},\text{hv}}} (c_{\text{NO},\text{in}} - c_{\text{NO},\text{out}}) \cdot \Delta t \quad (3)$$

$$n_{\text{des}} = \frac{p\dot{V}_{\text{air}}}{RT} \cdot \sum_{t_{\text{E},\text{hv}}}^{t_{\text{E}}} c_{\text{NO},\text{out}} \cdot \Delta t \quad (4)$$

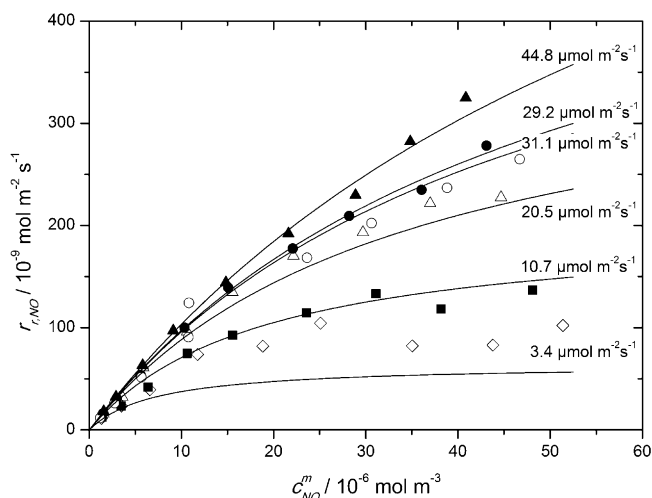
Fig. 3 shows a plot of the removed amount of NO ( $n_{\text{rem}}$ ) vs. the incoming NO concentration ( $c_{\text{NO},\text{in}}$ ) at different UV(A) light intensities. As can be seen from this figure, the removed amount of NO ( $n_{\text{rem}}$ ) is increasing with an increasing concentration of NO in the incoming gas stream ( $c_{\text{NO},\text{in}}$ ) and with an increasing light intensity. The experimental data presented in this figure reveal that at the light intensity stipulated by the standard operation procedure, i.e.,  $10 \text{ W m}^{-2}$  [35], the amount of NO removed from the gas phase by photocatalytic oxidation is strongly affected by small changes of the light intensity as well as of the NO concentration in the gas stream entering the photoreactor. Therefore, these parameters apparently



**Fig. 2.** Time course of the NO concentration at the reactor outlet observed during a typical experimental run with an UV(A) irradiated Aeroxide® TiO<sub>2</sub> P25 sample.



**Fig. 3.** Dependence of the photocatalytically removed amount of NO ( $n_{\text{rem}}$ ) vs. the incoming NO concentration ( $c_{\text{NO},\text{in}}$ ) at different UV(A) light intensities. Trendlines are included to guide the eye.



**Fig. 4.** Dependence of the photocatalytic reaction rate on the mean NO concentration inside the photoreactor at different UV(A) light intensities. The lines have been calculated using Eqs. (17)–(19) and  $k_r\eta = 18.9 \cdot 10^{-3}$ ,  $k_{ads} = 12.1 \cdot 10^{-3} \text{ m}^{-2} \text{ s}^{-1}$ , and  $k_{des} = 22 \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ .

have to be controlled very carefully to obtain correct results with this standard test.

At a light intensity of  $15 \text{ W m}^{-2}$  an almost linear increase of the removed amount of NO with increasing NO inlet concentration was observed. On the other hand, at a light intensity of  $1 \text{ W m}^{-2}$  the removed amount of NO seems to be independent from the NO inlet concentration at  $c_{\text{NO},in} > 20 \mu\text{mol m}^{-3}$ . This unexpected behaviour obviously requires an explanation.

While no steady-state concentration of NO at the reactor outlet was reached even after 2 h of continuous illumination (cf. Fig. 2: the NO concentration is slightly but continuously increasing during the entire duration of the UV(A) irradiation) an average rate of the photocatalytic reaction was calculated by dividing the total removed amount of NO ( $n_{rem}$ ) by the geometric photocatalytically active surface area  $A$  of the sample and the irradiation time  $\Delta t_{irr}$ :

$$r_{r,\text{NO}} = \frac{n_{rem}}{A \Delta t_{irr}} \quad (5)$$

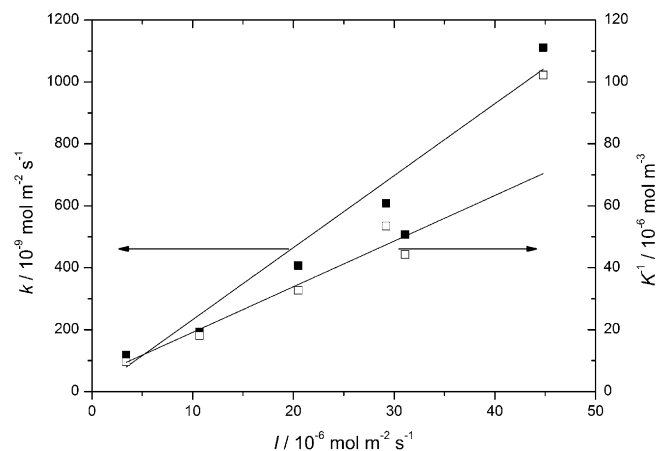
Since in the type of photoreactor employed in this study a gradient of the NO concentration over the photocatalyst surface in the direction of the gas flow is present during UV(A) irradiation the experimental data were analyzed by plotting the average reaction rate vs. the mean NO concentration inside the photoreactor ( $c_{\text{NO}}^m$ ). The mean NO concentration was calculated from the measured concentrations by

$$c_{\text{NO}}^m = \frac{1}{2N} \sum_N (c_{\text{NO},in} - c_{\text{NO},out}) \quad (6)$$

The standard deviation for  $c_{\text{NO}}^m$  was smaller than 8% in all experimental runs. Plots of the reaction rates vs. the mean NO concentrations inside the photocatalytic reactor are given for different light intensities in Fig. 4. It is obvious from the results shown in this figure that the reaction rates are increasing at a given light intensity with increasing NO concentration inside the photoreactor finally approaching a limiting value that clearly depends upon the light intensity.

The obtained experimental data can be fitted rather well employing a Langmuir–Hinshelwood-type rate law

$$r_{r,\text{NO}} = \frac{k \cdot K \cdot c_{\text{NO}}^m}{1 + K \cdot c_{\text{NO}}^m} \quad (7)$$



**Fig. 5.** Plot of the kinetic parameters  $k$  and  $K^{-1}$  vs. the photon flux  $I$ .

which has previously been used by several authors to describe the kinetics of the photocatalytic degradation of nitrogen(II) oxide in the gas phase [9,20,25,27].

Using Eq. (7) and the data given in Fig. 4 the kinetic constants  $k$  and  $K$  were calculated for each light intensity (cf. Table 1). The data presented in this table clearly show that both constants, i.e.,  $k$  and  $K$ , vary considerably with the employed light intensity.

A plot of  $k$  and  $K^{-1}$  vs. the incident UV(A) photon flux is presented in Fig. 5 evincing within the statistical errors of the experimental values that both, the kinetic parameter  $k$  ( $k = k(I) = \text{const} \times I$ , correlation coefficient = 0.980) as well as the reciprocal value of the parameter  $K$  depend linearly on the photon flux ( $K^{-1} = K(I)^{-1} = \text{const}(1) \times I + \text{const}(2)$ , correlation coefficient = 0.911). The analysis of the data presented in Table 1 by non-linear regression analysis resulted in  $k(I) \approx I^{(0.86 \pm 0.14)}$  and  $K(I) \approx I^{-(0.94 \pm 0.15)}$ , thus supporting the derived linear relation between  $k$  and  $K^{-1}$ , respectively, and the photon flux.

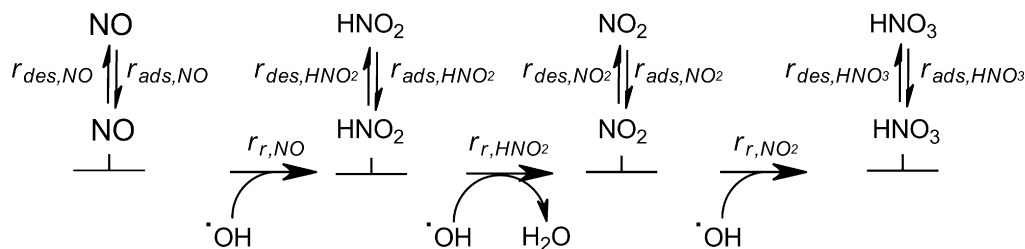
The values obtained here for  $k(I)$  and  $K(I)$  (cf. Table 1) deviate significantly from the values recently published for  $\text{TiO}_2$ -coated woven glass fabrics ( $k = 2.28 \cdot 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$  and  $K = 341 \text{ m}^3 \text{ mol}^{-1}$ ) [20] but are in good agreement with values reported for photocatalytically active concrete ( $k = (7\text{--}27) \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$  and  $K = (107\text{--}195) \cdot 10^3 \text{ m}^3 \text{ mol}^{-1}$ ; calculated from the data presented in [27]). It is worth noting that an increase of  $k$  and a decrease of  $K$  with increasing light intensity were also observed for the latter material [27].

The photocatalytic oxidation of NO is usually assumed to be a surface reaction between NO and an oxidizing species formed upon the adsorption of a photon by the photocatalyst, e.g., a hydroxyl radical, both adsorbed at the surface of the photocatalyst [27]. It has been shown by various authors that the final product of the photocatalytic oxidation of NO in the presence of  $\text{TiO}_2$  as the photocatalyst is nitric acid ( $\text{HNO}_3$ ) while  $\text{HNO}_2$  and  $\text{NO}_2$  have been identified as intermediate products in the gas phase over the photocatalyst [12–14,18]. The resulting reaction pathway of the photocatalytic oxidation of NO has been discussed in several publications [7–9,18–20,28] most of which proposed the photocatalytic conversion of NO via  $\text{HNO}_2$  to yield  $\text{NO}_2$ , which is subsequently oxidized by the attack of a hydroxyl radical to the final product  $\text{HNO}_3$ . Reductive processes, the possibility of homogeneous reactions in the gas phase between NO and photocatalytically produced reactive species desorbed from the photocatalyst surface, and secondary reactions between nitrogen compounds in the gas phase and/or at the photocatalyst surface are usually not considered. Based on these considerations the reaction pathway given in Fig. 6 is proposed where all nitrogen compounds adsorbed at the photocatalyst surface are in equilibrium with the gas phase.

**Table 1**  
Calculated kinetic parameters  $k(I)$  and  $K(I)$  for different photon fluxes I.

1	2	3	4	5
$I$ ( $10^{-6}$ mol m $^{-2}$ s $^{-1}$ )	$k(I)$ ( $10^{-9}$ mol m $^{-2}$ s $^{-1}$ )	$K(I)$ ( $10^3$ m $^3$ mol $^{-1}$ )	Calculated using Eqs. (17)–(19) <sup>a</sup>	
			$k(I)$ ( $10^{-9}$ mol m $^{-2}$ s $^{-1}$ )	$K(I)$ ( $10^3$ m $^3$ mol $^{-1}$ )
3.4 ± 0.4	117 ± 14	104 ± 39	64	139
10.7 ± 0.1	192 ± 18	55.2 ± 12.3	203	53.8
20.5 ± 0.2	407 ± 25	30.6 ± 3.5	388	29.5
29.2 ± 0.9	608 ± 48	18.7 ± 2.2	553	21.0
31.1 ± 0.5	507 ± 67	22.6 ± 5.1	589	19.8
44.8 ± 1.5	1111 ± 190	9.78 ± 2.17	848	13.9

<sup>a</sup> Calculated employing Eqs. (17)–(19) and  $k_r \eta = 18.9 \cdot 10^{-3}$ ,  $k_{ads} = 12.1 \cdot 10^{-3}$  m s $^{-1}$ , and  $k_{des} = 22 \cdot 10^{-9}$  mol m $^{-2}$  s $^{-1}$ .



**Fig. 6.** Proposed reaction steps during the photocatalytic oxidation of NO to yield HNO<sub>3</sub>.

In the attempt to explain the influence of the light intensity on the kinetic parameters  $k$  and  $K$  (as shown in Fig. 5) a steady-state approach, originally suggested by Ollis [37], has been used here to derive a rate law of the photocatalytic degradation of NO:

$$r_{ads,NO} - r_{r,NO} - r_{des,NO} = 0 \quad (8)$$

The rate of the adsorption of NO at the photocatalyst surface ( $r_{ads,NO}$ ), the rate of the photocatalytic reaction of the adsorbed NO ( $r_{r,NO}$ ), and the rate of desorption of NO from the surface ( $r_{des,NO}$ ) are defined by Eqs. (9)–(11):

$$r_{ads,NO} = k_{ads,NO} \cdot \Theta_{free} \cdot c_{NO} \quad (9)$$

$$r_{r,NO} = k_r \cdot \Theta_{NO} \cdot \Theta_{Ox} \quad (10)$$

$$r_{des,NO} = k_{des,NO} \cdot \Theta_{NO} \quad (11)$$

Concurrent adsorption between the nitrogen compounds NO, HNO<sub>2</sub>, NO<sub>2</sub>, and HNO<sub>3</sub> is assumed. Hence, the fraction of free adsorption sites at the photocatalyst surface is given by

$$\Theta_{free} = 1 - \Theta_{NO} - \Theta_{HNO_2} - \Theta_{NO_2} - \Theta_{HNO_3} \quad (12)$$

Since the concentration of the NO oxidation products, i.e., HNO<sub>2</sub>, NO<sub>2</sub>, and HNO<sub>3</sub> in the gas phase is rather low as compared with  $c_{NO}$ , desorption of these compounds is assumed to be the preferred process, and

$$\Theta_{HNO_2} + \Theta_{NO_2} + \Theta_{HNO_3} = 0 \quad (13)$$

can be taken as a first approximation; therefore, the amount of free adsorption places is given by Eq. (14):

$$\Theta_{free} = 1 - \Theta_{NO} \quad (14)$$

In Eq. (10),  $\Theta_{Ox}$  represents the coverage of the photocatalyst surface by oxidizing species, e.g., hydroxyl radicals formed by surface trapped holes and  $O_2^{\bullet-}/HO_2^{\bullet}$  formed by electrons trapped at preadsorbed  $O_2$ -sites. In accordance with the experimental data presented above, the coverage of the photocatalyst surface by those oxidizing species is assumed to be directly proportional to the flux  $I$  of the incoming UV(A) light:

$$\Theta_{Ox} = \eta \cdot I \quad (15)$$

It was shown by Imoberdorf et al. that Eq. (15) is one limiting case of a more general expression describing the influence of the photon flux on the coverage  $\Theta_{Ox}$ , which has been derived by Upadhy and Ollis [38,39]. Losses by the reflection of light and the recombination of the charge carriers are considered by the efficiency factor  $\eta$ , which combines different parameters describing, e.g., the charge carrier recombination in the bulk and/or on the surface of the photocatalyst, the adsorption equilibrium of water and molecular oxygen at the photocatalyst surface, the interfacial electron transfer rate and efficiency, and the light absorbing properties of the photocatalyst [38,39].

Inserting Eqs. (9), (10), (11), (14), and (15) into Eq. (8) yields after rearrangement an equation for the surface coverage by NO:

$$\Theta_{NO} = \frac{k_{ads} c_{NO}}{k_{des} + k_r \eta I + k_{ads} c_{NO}} \quad (16)$$

By inserting Eqs. (15) and (16) into Eq. (10) and taking  $c_{NO} = c_{NO}^m$  a rate law for the photocatalytic degradation of NO is obtained as follows:

$$r_{r,NO} = \frac{k(I) \cdot K(I) \cdot c_{NO}^m}{1 + K(I) \cdot c_{NO}^m} \quad (17)$$

with

$$k(I) = k_r \eta \cdot I \quad (18)$$

and

$$K(I) = \frac{k_{ads}}{k_{des} + k_r \eta \cdot I} \quad (19)$$

Using these equations  $k_r \eta = 18.9 \cdot 10^{-3}$ ,  $k_{ads} = 12.1 \cdot 10^{-3}$  m s $^{-1}$ , and  $k_{des} = 22 \cdot 10^{-9}$  mol m $^{-2}$  s $^{-1}$  (correlation coefficient = 0.988) are obtained by non-linear regression analysis of the experimental data presented in Fig. 4, neglecting the data obtained at a photon flux of  $3.4 \mu\text{mol m}^{-2} \text{s}^{-1}$ . As can be seen from Table 1 for this average light intensity the calculated photon flux is afflicted by a standard deviation of more than 10% while the standard deviation in all other cases is smaller than 3%. The deviation between the kinetic parameters derived from the experimental data (cf. rows 2 and 3 in Table 1) and the respective values of  $k(I)$  and  $K(I)$  calculated employing Eqs. (17)–(19) (cf. rows 4 and 5 in Table 1) is less than 15% except



for the low photon flux of  $3.4 \mu\text{mol m}^{-2} \text{s}^{-1}$  and the high photon flux of  $44.8 \mu\text{mol m}^{-2} \text{s}^{-1}$ . Possible reasons for these observed deviations are the lack of precision in the experimental determination of low light intensities and missing experimental data in the plateau region at  $c_{\text{NO}}^m > 45 \mu\text{mol m}^{-3}$  at the high photon flux of  $44.8 \mu\text{mol m}^{-2} \text{s}^{-1}$ . Nevertheless, the calculated curves in Fig. 4 model fairly well the general dependence of the experimentally obtained reaction rates from the NO concentration inside the photoreactor as well as from the incident photon flux. The comparison of the experimental data with the values calculated with the kinetic parameters given above (cf. Fig. 4) reveals a rather good agreement between the reaction rates predicted by the kinetic model and the rates determined from the experiments performed at higher photon fluxes. Deviations between the experimental and the calculated data can as already mentioned be attributed to the inaccuracy in the determination of the photon flux particularly at low light intensities, as well as to the limited set of experimental data available for the data analysis in this study. Eqs. (17)–(19) can obviously be employed to explain the observed dependence of the reaction rate on the NO concentration at different light intensities.

According to the derived values for  $k_{\text{ads}}$ ,  $k_{\text{des}}$  and  $k_r\eta$ , at a low photon flux of  $3 \mu\text{mol m}^{-2} \text{s}^{-1}$  the coverage of the  $\text{TiO}_2$  surface with adsorbed NO molecules is only changing by 17% from 0.75 to 0.88 when the NO concentration inside the photoreactor increases from 20 to  $50 \mu\text{mol m}^{-3}$ . Hence, only a small increase of the reaction rate with increasing NO concentration is expected at this photon flux. On the other hand, at a high photon flux of  $45 \mu\text{mol m}^{-2} \text{s}^{-1}$  the coverage is predicted to change by 86% from 0.22 to 0.41 when the NO concentration increases from 20 to  $50 \mu\text{mol m}^{-3}$  resulting in a pronounced increase of the reaction rate. At  $c_{\text{NO}}^m = 40.9 \mu\text{mol m}^{-3}$  (1 ppm) and a photon flux of  $29.7 \mu\text{mol m}^{-2} \text{s}^{-1}$  ( $10 \text{ W m}^{-2}$ ) the coverage of the titanium dioxide surface with NO is calculated to be 0.46. A change of the NO concentration or the photon flux by 10% will, under these conditions, result in a change of the coverage  $\theta_{\text{NO}}$  of about 5%.

The rate law derived in this study (Eq. (17) with (18) and (19) was moreover successfully applied to analyze the values for  $k$  and  $K$  published by Hunger et al. for the photocatalytic oxidation of NO at an UV(A) irradiated  $\text{TiO}_2$  containing concrete surface [27]. The parameters obtained from the linear Eqs. (18) and (19) (correlation coefficients = 0.981 and 0.835, respectively, for  $k=f(I)$  and  $K^{-1}=f(I)$ ) are  $k_r\eta=0.95 \cdot 10^{-3}$ ,  $k_{\text{ads}}=5.8 \cdot 10^{-3} \text{ m s}^{-1}$ , and  $k_{\text{des}}=28 \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ .

It should, however, be clearly stated here, that the model employed here is (just like any other scientific model) based upon several assumptions and simplifications – one of them being that NO is the only nitrogen-containing species that is adsorbed on the photocatalyst surface to any appreciable extend.

#### 4. Conclusions

The standard test procedure described in ISO 22197-1, which was developed to characterize the photocatalytic activity of air-cleaning products, was successfully applied to determine the photocatalytic activity of a bare  $\text{TiO}_2$  powder. The experimental data reveal that at the light intensity stipulated by the operation procedure, i.e.,  $10 \text{ W m}^{-2}$  ( $I=29.7 \mu\text{mol m}^{-2} \text{s}^{-1}$ ), the amount of NO removed from the gas phase by photocatalytic oxidation is strongly affected by rather small changes of the light intensity as well as of the NO concentration in the gas phase present in the photoreactor. Therefore, these parameters have to be controlled very carefully.

Based upon the analysis of the experimental data obtained in this study a rate law was derived which allows the prediction of the reaction rate of the photocatalytic NO oxidation at varying NO concentration and photon fluxes.

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