Article
Methodology for Simultaneous Analysis of Photocatalytic deNO$_x$ Products

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Abstract: The ISO standard 22197-1:2016 used for the evaluation of the photocatalytic nitric oxide removal has a main drawback, which allows only the decrease of nitric oxide to be determined specifically. The remaining amount, expressed as "NO$_2$", is considered as a sum of HNO$_3$, HONO NO$_2$, and other nitrogen-containing species, which can be potentially formed during the photocatalytic reaction. Therefore, we developed a new methodology combining our custom-made analyzers, which can accurately determine the true NO$_2$ and HONO species, with the conventional NO one. Their function was validated via a photocatalytic experiment in which 100 ppbv of either NO or NO$_2$ dispersed in air passed over (3 L min^{-1}) an Aeroxide© TiO$_2$ P25 surface. The gas-phase analysis was complemented with the spectrophotometric determination of nitrates (NO$_3^-$) and/or nitrites (NO$_2^-$) deposited on the P25 layer. Importantly, an almost perfect mass balance (94%) of the photocatalytic NOx abatement was achieved. The use of custom-made analyzers enables to obtain (i) no interference, (ii) high sensitivity, (iii) good linearity in the relevant concentration range, (iv) rapid response, and (v) long-term stability. Therefore, our approach enables to reveal the reaction complexity and is highly recommended for the photocatalytic NOx testing.

Keywords: photocatalysis; air purification; NOx; HONO; NO$_2$; mass balance

1. Introduction

Nitrogen oxides (NOx) present in the air are considered to be toxic gases. There exist several strategies for NOx removal, focusing either on the emission control and prevention of their formation, or dealing with NOx conversion to N$_2$ or HNO$_3$ using additional chemical reagents [1]. While these methods cannot be used for NOx concentration of parts per billion (ppbv), heterogeneous photocatalysis offers such a possibility [2–5].

Because of the need to compare the performance of photocatalysts and assess their environmental applicability, the standard tests for the air-purification performance of semiconductor photocatalytic materials were developed, namely ISO 22197-1:2016, CEN (CEN/TS 16980-1, 2016), and UNI standards for nitric oxide (UNI 11247, 2010 and UNI 114874, 2013), further referred as ISO, CEN, and UNI.

Although these methods are well designed and allow the interlaboratory comparison of results in terms of photocatalytic activity, they are less meaningful for the prediction of the actual environmental impact under real-world conditions. The high input concentration of 500–1000 ppbv NO is one order of magnitude higher than that in heavily polluted air. Only NO is used as the model pollutant (except UNI 11247, 2010), although NO$_2$ is more toxic (its amount in air is restricted by specific limit). While the NOx analyzer (chemiluminescent) specified in ISO 7996 measures only NO selectively, NO$_2$ measurement suffers from the interference of other N-containing gases, including HONO and HNO$_3$.

Thus, to evaluate the real impact of NO_x photocatalytic abatement technology, a complete analysis of the degradation intermediates and products even at their very low concentration is of utmost importance. Such analytical data will enable to proceed with a complete balance of NO_x compounds. This is necessary for the realistic assessment of the performance of photocatalytic technology.

To address this issue, several strategies were reported (Table S1). Ifang et al. [6] suggested testing the photocatalytic activity under relevant atmospheric conditions and low reactant concentrations (<100 ppbv), and strongly recommended NO_2 as a tested reactant. According to the authors, the yield of nitrate formed by the photooxidation of NO_2 should be quantified by ion chromatography to exclude or confirm the formation of other N-containing products. The interference issues of chemiluminescence analyzers can be solved by using carbonate denuder as a trap for HONO [7].

Besides the common detection of NO and NO_2, several papers have dealt with the detection of other N-containing species. A chemiluminescence method for the detection of HONO was reported [8]). Alternatively, HONO was detected by employing the long-path absorption photometer (LOPAP) method [9,10] developed by Heland et al. [11]. The detection of NO_2, HONO, and N_2O by the combination of selective catalytic conversion measurement, LOPAP, and the gas chromatography/electron-capture detector, respectively, was published [12]. Furthermore, these studies also focused on the determination of nitrate (NO_3^-) and nitrite (NO_2^-) anions adsorbed on the surfaces using ion chromatography. N_2O detected by GC-MS with cryotrapping was found to be the main product from the NO reactant; however, the NO concentration was 100 ppmv, i.e., very high [13].

The analysis of the all-important N-compounds (NO, NO_2, HONO, HNO_3, and N_2O) needed for the overall evaluation of photocatalyst performance is still exceptional within the research community. Dedicated research dealing with possible solutions of complete NO_x degradation monitoring and photocatalytic activity assessment is of great value.

Therefore, we developed a methodology for the continuous monitoring of N-species participating in photocatalytic NO_x abatement. Our novel complex apparatus is partly based on the ISO standard (NO analyzer, bed-flow reactor, total reactor flow, light intensity, humidity) in order to enable interlaboratory results; however, we have supplemented it with very sensitive and selective NO_2 and HONO analyzers. After optimization procedures, the determination of the full balance of N-products ($N^{+2,3,4,5}$) was carried out, including those adsorbed in the photocatalyst (HNO_3 and HONO). This enabled us to assess more realistically the possible environmental impact of the air purification by means of photocatalysts.

2. Results and Discussion

2.1. Requirements to the Apparatus

There are a number of requirements which should be fulfilled. We show that our analytical system used in the developed experimental set-up fulfills following requirements:

1. No interference with each other;
2. Sufficient sensitivity achieving low detection limit;
3. Good linearity of the response in the needed concentration range;
4. Rapid response;
5. Long-term stability–suppressed zero drift;
6. Reasonable investment and operating costs.

Ad 1: Analyzers connected in parallel must not interfere with each other. Specifically, the analyzers must not exhibit chemical interferences towards other N-containing species. It is desirable to test independently the proper function of each analyzer and perform their calibration. This is realized by a system of three-way valves, as specified below. The whole apparatus tightness is crucial due the toxic gases used, and any leaks must be revealed easily. Therefore, the system should be well-arranged and sufficiently easy to operate. Apparatus materials have to be inert for all the used chemicals, and the tubes should be as short as possible to minimize the sorption of the gases. Chemiluminescence analyzers

(HONO and NO_2) were tuned to be interference-free [14–16]. The NO_2 analyzer showed no detectable response to 1.0 ppmv of NO, and the HONO analyzer showed no detectable response both to 100 ppbv NO_2 and NO.

Ad 2: Due to the very low concentrations to be monitored, a high sensitivity of analyzers is essential. Techniques based on chemiluminescence detection fulfill this requirement very well. The advantages of chemiluminescence techniques lie in their selectivity as well as very good sensitivity. The sensitivity (and the dynamic range) can be optimized by the composition of the chemiluminescence solutions as well as by the gas flow through the analyzer.

The detection limit ought to be in units of ppbv, as it usually occurs in natural air. The nominal detection limits of the NO_2 and HONO analyzers according to the producers are much lower than is needed for our application [14–16]. However, the detection limits determined in our laboratory with the analyzers connected to the measurement system were much higher: 6.0 ppbv for NO_2 and 1.0 ppbv for HONO. Meaningful reasons may be the additional instabilities caused by parallel sampling and the additional adsorption of gases within the tubes. The limit of detection was estimated as the concentration at which the signal would be equal three-times the standard deviation of the background signal.

Ad 3 and 4: For the possible application in kinetic studies, it is crucial that the analyzers respond rapidly with a sufficient frequency of data collection at least in one-second intervals. Furthermore, the response needs to be linear over the range of expected concentrations ranged from 1.0 to 1000 ppbv. For the HONO analyzer, a good linearity was found in the tested range 2.0–300 ppbv. The NO_2 analyzer performed a linear trend for concentrations ranging from 10 to 1000 ppbv. Below 10 ppbv, nonlinearity was observed, as was previously described in the literature [15].

Ad 5: A critical parameter for the applicability of the selected techniques is their long-term stability. For the chemiluminescence custom-made analyzers, it was tested with following concentrations: 100 ppbv for NO_2 and 34 $\mu g\ L^{-1}$ for NO_2^- (corresponding to 12 ppbv of HONO in the air under given experimental conditions). The dosing of the chemicals by peristaltic pumps may be unstable for longer time periods. Therefore, for NO_2, the stability was evaluated by observing the averages of the signals by periods of 10 min (122 points) within 10 h, with the standard deviation of those averages being less than 1%. For HONO, the signal was averaged for 5 min before and after 8 h of the photocatalytic experiment (signal obtained from standard solution of NO_2^-), the difference being 1.5%. Both custom-made analyzers showed acceptable stability during a time period of at least 8 h, which is sufficient to ensure a reliable assessment of the photocatalytic activity.

Ad 6: The investment needed for assembling the custom-made analyzers is given mainly by the cost of the photomultiplier and the pumps (for liquid reagents and gas sampling). From current prices of these components, the estimated cost is below EUR 4000. This is roughly five times lower than the cost of a commercial NO_2 analyzer. Currently, commercial analyzers for HONO have not been developed.

2.2. Photocatalytic Reactor and Analytical System

Our self-developed set-up consisted of three main parts: a gas supply manifold, a photoreactor, and an analytical system (Figure 1). A set of mass flow controllers (Bronkhorst, The Netherlands) was used to dilute the pollutant (50 ppmv NO or NO_2 in N_2, Messer Technogas, Prague, Czech Republic) to the desired concentrations of 100 and 1000 ppbv. The carrier gas (synthetic air) was humidified using a Drechsel bottle. Stream of the gas passed through the photoreactor (ISO 22197-1, 2016) over a photocatalyst layer. Specifically, the following testing conditions have been retained: total flow rate 3 L min^{-1}, relative humidity 50% at 25 °C, radiation intensity 1.0 mW cm^{-2} of UVA light (TL-D 15W BLB, Philips, Prague, Czech Republic) with a dominant wavelength at 365 nm, a geometric area of the layer 5 × 10 cm^2, and the space height of 0.5 cm above the layer for the flowing gas. The output of the reactor was divided into branches leading to the analyzers for HONO,

NO$_2$, and NO$_x$/NO monitoring (Figure 1). These are described in the Supplementary Materials (Figures S1 and S2).
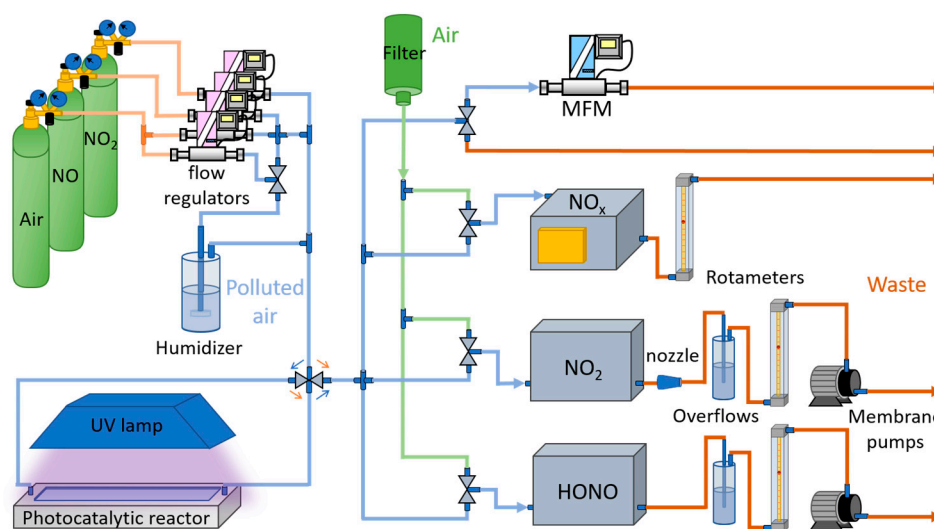

Figure 1. Set-up for testing the performance of photocatalysts for NOx abatement equipped with NO/NO$_x$, NO$_2$, and HONO analyzers.

Downstream of the reactor, the gas is simultaneously distributed to the analyzers. They actively suck the gas by pumps, which are protected by liquid overflow bottles placed in front of the pumps. The exhaust tubes downstream of the pumps are equipped by one-way valves, preventing the return of the exhaust gases. The inlet to each analyzer can be switched by a three-way ball valve between the analyzed gas and air from the lab drawn through a filter. The analyzers can thus be tested individually. The excess gas goes either directly to waste or can be passed by a 3-way ball valve through a capillary mass-flow meter (MFM) to test the leakages in the segment of the system, including the photoreactor. The bubbler has to be first bypassed to avoid damaging the MFM by water vapor.

2.3. Determination of Products in Gaseous Phase

The deNOx curves were integrated based on the formula in Equation (1), as follows:

$$deNOx = \frac{p(qx_{NOx\ in}t - \int_{t=0}^{t} qx_{NOx}dt)}{RT} \tag{1}$$

where p is normal gas pressure (101.325 kPa), q is the total gas flow (m^3 s^{-1}), t is the time of photocatalysis (s), $qx_{NOx\ in}$ is a molar fraction of the pollutant in the input gas mixture, x_{NOx} is the measured instantaneous NO$_x$ molar fraction in the gas mixture behind the photoreactor, R is the molar gas constant (8.314 J.K^{-1} mol^{-1}), and T is temperature (273.15 K). The gas conditions are given from the mass flow controllers, where the controlled volume flow is given under normal conditions.

2.4. Quantification of NO$_2^-$ and NO$_3^-$ Anions (HONO and HNO$_3$) Adsorbed on the Photocatalyst

Nitrite and nitrate anions accumulated on the layer during the photocatalytic reaction were determined by means of an ultralow-range colorimeter (HI764 Nitrite Checker, Hanna Instruments, Prague, Czech Republic) and corresponding reagents. After a 24 h extraction of the anions to an exact volume (60 or 80 mL) of deionized water, a proper dose of diazotation reagents (Hanna Instruments, Prague, Czech Republic) was added to the solution and stirred carefully. In the presence of NO$_2^-$ anions, the solution became a shade of pink, depending on the nitrite concentration. NO$_3^-$ anions were first reduced to NO$_2^-$ by cadmium (reagents NitraVer6, Hach Lange, GmbH, Berlin, Germany) and,

afterwards, analyzed by the equal procedure as for NO_2^-. Concentration values obtained for the nitrites were determined using the known $NaNO_2$ solution concentration, and those for nitrates were adjusted according to the measurement of the known KNO_3 solution concentration. In several cases, the solutions with the extracted nitrites/nitrates were analyzed spectrophotometrically in a commercial lab for comparison, and the results were in the reasonable agreement. Always fresh layers were used for these experiments.

2.5. Modified ISO Test Conditions

Unlike the standardized methods, we focused on the following experimental conditions. First, the inlet concentration of the model NO or NO_2 pollutant was adjusted to 100 ppbv, which corresponds to realistic environmental conditions. Due to simple reaction stoichiometry, the sum of the concentrations of all assumed gaseous N-compounds (NO, NO_2, HONO, HNO_3, but not N_2O) present in the air flow was expected to be the same as the initial concentration of reactant. The standard total gas flow (3 L min^{-1}) through the reactor maintained unmodified.

Second, the duration of the photocatalytic test was longer. Our experiments showed that for highly active samples, the steady-state was not reached even after five hours. Third, three analyzers were used, in contrast to the only one in the ISO standard.

3. Validation

3.1. Determination of Products in Gaseous Phase

To verify the proper functioning of the apparatus, the photocatalytic reaction of NO_2 was tested on the TiO_2 (P25) layer (49.1 mg). A model NO_2 pollutant with a concentration of 100 ppbv in the air with 50% relative humidity flowed through the reactor at a flow rate of 3 L min^{-1}. After purging the reactor and stabilizing the input concentration, the layer was irradiated with a UV lamp of an irradiation intensity of 1.0 mW cm^{-2}. At the very beginning of the photocatalytic reaction, the NO_2 concentration immediately sharply dropped to half of its initial value, while neither HONO nor NO were formed in the gas phase (Figure 2A). We can deduce that all the removed NO_2 was adsorbed onto the surface of the photocatalyst, mainly in the form of NO_2 and HNO_3. This explains the subsequent partial deactivation of photocatalyst in the first one hour [17]. After this period, the reaction achieved a steady-state character with a negligible change of NO_2 concentration (0.3 ppbv per hour).
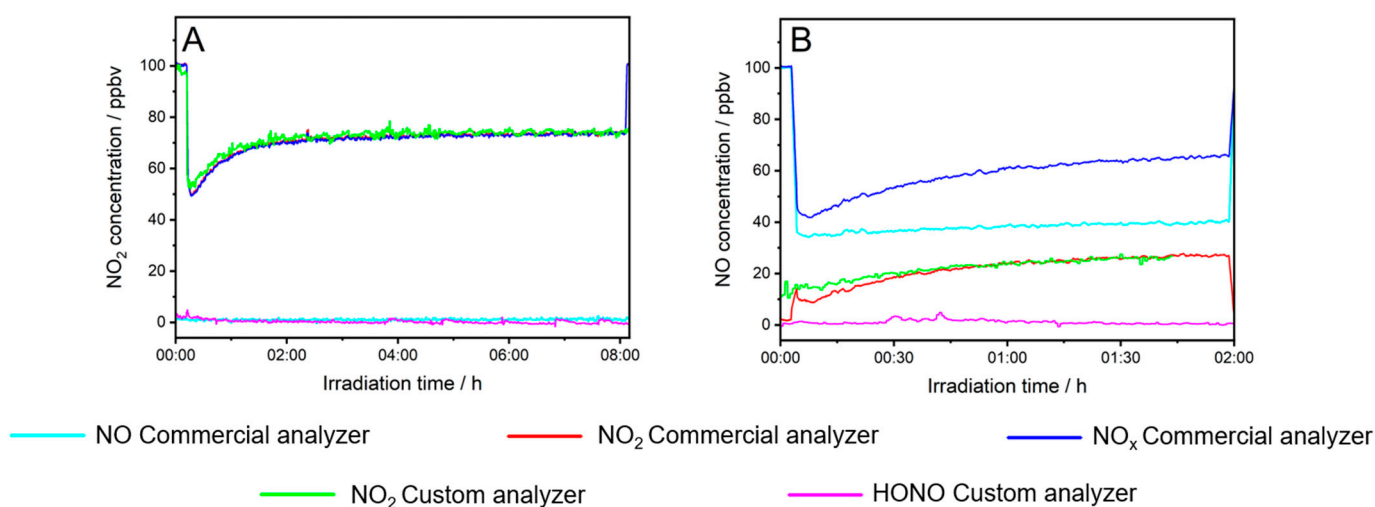

Figure 2. Set-up for testing the performance of photocatalysts for NOx abatement equipped with NO/NO$_x$, NO$_2$, and HONO analyzers. A 100 ppbv inlet concentration of NO$_2$ (**A**) and NO (**B**), respectively.

Measurement via a commercial analyzer (APNA-370, Horiba, Tokyo, Japan) was complemented with the selective measurement of NO_2 and HONO using our custom-made analyzers. In this case, the NO_2 measurements are in excellent agreement with the values obtained by the commercial APNA-370 (Figure 2A). This agreement can be associated with the negligible formation of gaseous HONO and HNO_3, which would otherwise contribute to the NO_2 and NOx signals of the APNA-370 analyzer.

Similar experiments were performed for 100 ppbv of NO while maintaining the same reaction conditions. The decrease in the NO concentration in the air to 40 ppbv caused by oxidation was accompanied by the gradual rise of the NO_2 concentration (Figure 2B). The NO_2 concentration measured by the custom-made NO_2 analyzer (Figure 2B, green line) is again in very good agreement with the NO_2 values obtained from the commercial one (Figure 2B, red line). A tiny discrepancy observed at the beginning of the experiment (up to 30 min) can be explained by the calibration of the custom-made NO_2 analyzer below 10 ppbv due to a nonlinear behavior, as well as to the detection limit (6.0 ppbv). Moreover, a negligible concentration of gaseous HONO was detected during the photocatalytic abatement of NO.

3.2. Determination of Products in Solid Phase

HNO_3 and HONO formation and their presence on the P25 layer were confirmed by the extraction, described in the Experimental section. Amounts of HONO were at least ten times smaller than those of HNO_3, since nitrite anions were mostly oxidized to nitrate during the layer transfer from the reactor and following the one-day extraction of anions into water. Commercial analysis by spectrophotometry found the nitrite anions to be three orders of magnitude less than the nitrate ones.

3.3. NOx Balance

Table 1 shows the comparison of the amount of NO_x removed from the gas stream and the HNO_3 deposited on the photocatalyst surface. From these data, the percentage imbalance p between the inlet, outlet, and deposited amount was evaluated according to Equation (2):

$$p = \left[\frac{(O + D) - I}{(O + D)} \right] \times 100 \ [\%] \qquad (2)$$

where O is outlet, D is deposited, and I is the inlet amount.

Table 1. A comparison of the amount of NO_x removed from the gas stream and HNO_3 deposited on the photocatalyst surface.

Pollutant	Irradiation Intensity/ mW cm^{-2}	Inlet Concentration/ ppbv	Total NO_x Passed over Photocatalyst [1]/ μmol	NO_x Removed from Gas Phase [2]/ μmol	HNO_3 Deposited on Photocatalyst [3]/ μmol
NO	0	100	3.68	0	<0.35
NO	1.0	100	3.68	0.65	0.90
NO_2	1.0	100	3.68	1.10	1.70
NO	1.0	1000	36.8	1.20	1.30

[1] in 5 h. [2] determined via integration of analyzer signal (after 5 h on stream). [3] determined via spectrophotometry of solid phase extraction (after 5 h on stream).

We observed that the amount of NO_x removed from the flowing gas determined by the integration of the analyzer signal is slightly lower than the amount of HNO_3 deposits (Table 1). For 100 ppbv of NO, and especially for 1000 ppbv NO, this imbalance is low, being 6 per cent, and practically negligible for the former and latter case, respectively. However, for 100 ppbv NO_2 in the inlet gas, the imbalance is higher, achieving about 14 per cent.

There exist several potential reasons for this difference. First, a shift of the analyzer output (e.g., due to a baseline instability). However, extensive tests showed that this is not the case, as the performance of the analyzer is stable and reproducible. Moreover, the

tightness of the set-up was checked by a helium test, and potential leaks can be completely excluded. Further, the sorption of NO_x on the walls of the set-up did not have any effect on the outcomes of the experiments, as the tests themselves were started after an equilibrium was achieved. At the same time, a potential content of nitrates or nitrites in the purchased TiO_2 powder was excluded by analytical measurement.

Second, the reason for the higher nitrate amount deposited on the photocatalyst may be the formation of nitrate by the oxidation of nitrogen in the carrier air on TiO_2. This speculation is supported by Yuan et al. [18], who observed such oxidation even by sunlight. Interestingly, we tested the possibility of a heterogeneous reaction of NO with the surface photocatalyst in the darkness at an inlet concentration of 100 ppbv; however, no formation of nitrates was detected.

Regarding the selection of either NO or NO_2 for the standard testing of the photocatalyst performance, an interesting conclusion follows. NO_2 seems more suitable due to its higher toxicity, and especially as a pollutant whose concentration is monitored according to relevant national limits and WHO guidelines. However, the imbalance given above shows that it is a rather problematic compound due to its chemical properties, such as complex sorption on the surface of not only the photocatalyst but also of other parts of the experimental set-up in contact with the polluted air. These complex relations were observed by Araña et al. [19], who determined the role of its sorption or disproportionation in producing NO. Another observed process was the formation of stable $[(NO_3^-)-(H_2O)-NO_2]$ complexes on the surface of the photocatalyst.

4. Preparation of TiO_2 Layers

For photocatalytic testing the commercial Aeroxide P25 (Evonik Industries, Essen, Germany, batch No. 616000298) was chosen. The surface of 5×10 cm^2 glass substrate was abraded by silicon carbide of grits 220 (Top Geo Mineralienhandel GmbH, Satteldorf, Germany) to increase the adhesion of ordinary soda-lime glass. Water suspension with 10 wt.% TiO_2 was homogenized by dispersing instrument T25 (IKA, Staufen, Germany) for 5 min at 20,000 rpm. This suspension was applied on the glass plate using an airbrush (PME, Enfield, UK) in multiple layers to achieve the required sample weight (50 mg). After spraying, each individual layer was dried with a blow dryer. All layers were stored in a dark chamber under the nitrogen atmosphere. Figure 3 confirms the homogeneity of deposited layers.
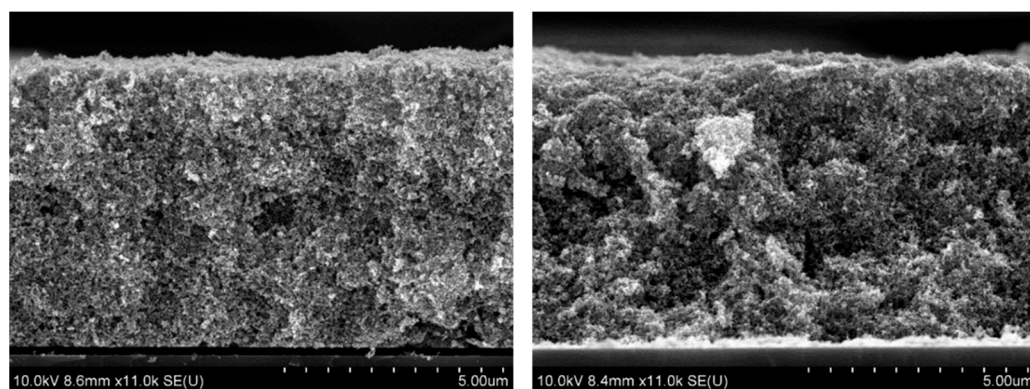

Figure 3. SEM micrographs of multiple P25 layer profiles. Left side–fivefold spraying. Right side–elevenfold spraying. In both, the same amount of TiO_2 deposited, and consequently the thickness of the multilayer is the same.

5. Conclusions

We have developed a new methodology for a broader assessment of the photocatalytic removal of NOx species in the air. Our custom-made analyzers, complemented with the conventional one, exhibited high performance in the simultaneous detection of the

true NO_2, HONO, and NO species during the photocatalytic NOx degradation. This innovative set-up enables to reliably determine a mass balance of the NO_x abatement when the analysis of deposits on the photocatalyst surface is involved. By our approach, almost perfect mass balance for NO (94%) and NO_2 (86%) removal was achieved. Furthermore, our study provides important suggestions concerning the suitability of NO and NO_2 as test molecules, with NO being more suitable. As a next step of our research, the upgrade of the photocatalytic apparatus by the implementation of a custom-made HNO_3 analyzer will follow.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal12060661/s1, Figure S1: Custom-made analytical system for HONO detection in air, designed and assembled by Mikuska and co-workers, Figure S2: Custom-made analytical system for NO_2 detection in air, designed and assembled by Mikuska and co-workers. Table S1: Overview of the analytical systems used to determine gaseous nitrogen-based species and ozone. Ref. [20] is cited in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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