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Supplement

Temperature Dependencies of the Degradation of NO, NO_2 and HONO on a Photocatalytic Dispersion Paint

Daniela Pill, Peter Wiesen and Jörg Kleffmann*

S1 Photocatalytic Paint

The used paint (StoPhotosan NOx dispersion paint, white) was already applied in a former study[1] and showed a high photocatalytic activity against NO, NO_2 and HONO. The photocatalyst used (Kronos Int.: vlp 7000) is a carbon doped titanium dioxide in Anatase modification. As specified by the manufacturer the photocatalyst displays photoactivity not only under UV but also under visible light (<500 nm). The paint is composed of an organic binder system which was optimized for low oxygenated VOC emissions[2] and contains a few wt % of the photocatalyst and 15 % of a non-catalytic TiO_2 in Rutil modification to obtain higher opacity. The pH of the paint is in the range 8 - 8.5.

The paint was hand-brushed on one side of a PVC (polyvinyl chloride) plate (49 mm × 99 mm × 8 mm) and the sample was already in regular use for several years in the laboratory. Before each experiment the surface was carefully washed with Millipore water, dried under nitrogen and irradiated overnight by two fluorescence tubes (λ_{max} = 365 nm) with an UVA irradiance of 33 W m^{-2} to decompose possible adsorbed impurities und to obtain more reproducible results.

S2 Photoreactor

The photocatalytic activity of the sample was studied in a temperature controlled flow photoreactor, which is adapted to ISO 22197-1,[3] see Fig. S1 and Fig. S2. As recommended by ISO, the sample bed has a dimension of 50 mm × 100 mm. However, in contrast to the ISO standard, the geometry of the reactor, the experimental conditions and the data evaluation were significantly improved, as explained in detail elsewhere.[4] The reactor consists of an upper cap made by PVC, which contains the inlet and exit for the gas mixture (with each 6 evenly spread inlet/exit holes), the UVA transparent Pyrex glass window and a thermocouple for surface temperature measurements. The lower sample holder is made by aluminum, which contains variable spacers to adjust the distance of the sample to the Pyrex window for variable

sample sizes. The sample holder is temperature controlled in the range 5-60°C by flushing water through channels in the aluminum block using an external thermostat (Thermo-Haake DC10-K10). Before the gas mixture enters the reactor, it is thermally equilibrated to the reactor temperature via a 1/8'' (o.d.) PFA line, which is tightly fixed in a meandering cut-out channel in the aluminum block, covered by an aluminum plate. The entire reactor and the water lines from and to the thermostat are insolated by Armaflex foam.

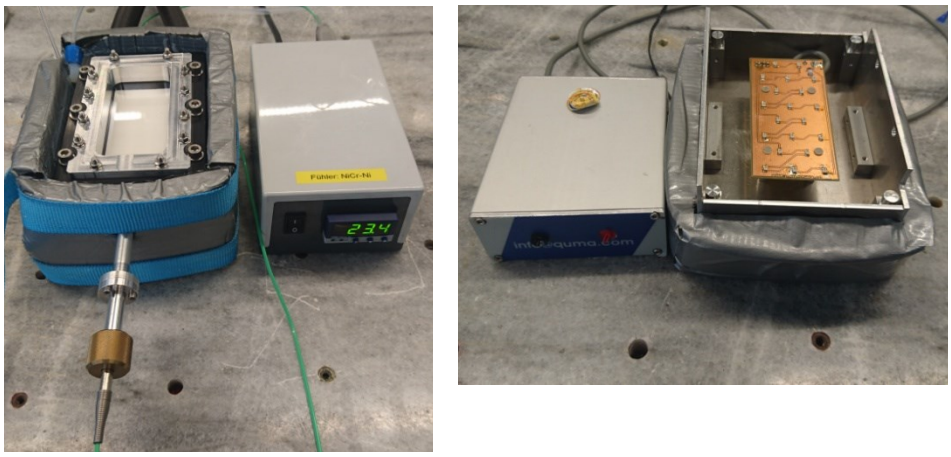

Fig. S1: Left: Turbulent flow photoreactor with thermocouple device for surface temperature measurements. Right: UV-diode array with power supply, 1-16 W m^{-2}; λ_{max} = 370 nm; $\Delta\lambda$ ± 20 nm (QUMA-Elektonik & Analytik, Wuppertal).

The flow conditions in the reactor are turbulent and not laminar to avoid transport limitations of the standard ISO method for fast uptake kinetics.[4,5] This is achieved by blowing the gas mixture via the 6 inlet holes towards a turbulence barrier directly in front of the sample, forming "lee-wave" turbulences on the sample. In addition, for the present study the distance between the sample and the window was only 1-2 mm (ISO 5 mm) leading to higher gas velocities. Since the hand-brushed paint showed also significant surface roughness (~±0.5 mm), the turbulent flow conditions were maintained over the whole sample surface without using additional turbulence barriers, as recommended in Ifang et al..[4] This was verified by varying the sample/window distance (*h*), for which the uptake is independent of *h*, see equation (I), in the absence of transport limitations. When reducing the reactor volume (decreasing *h*), the lower reaction time is exactly compensated by the increasing surface to volume (*S*/*V*) ratio.

In contrast to the original ISO method, which considers zero order kinetics,[3] uptake coefficients for NO, NO_2 and HONO were calculated assuming first order kinetics:

(I) $$\gamma = \frac{4 \cdot ln\left(\frac{c_{t=0}}{c_t}\right) \cdot \Phi_g}{S \cdot \bar{v}}$$,

for which $c_{t=0}$ and c_t are the mixing ratios [ppb] at the inlet and exit of the photoreactor, respectively, Φ_g is the gas flow rate [$cm^3\ s^{-1}$], S the surface area of the sample [cm^2] and $\bar{v}$ the average velocity of the reactants [$cm\ s^{-1}$] according to the gas kinetic theory ($\bar{v} = (8 \cdot R \cdot T \cdot \pi^{-1} \cdot M^{-1})^{0.5} \cdot 100$; with R=8.314 J mol^{-1} K^{-1}, T: absolute temperature [K] and M: molar mass [kg mol^{-1}]). First order kinetics was verified by changing the gas flow rate and the concentrations of the reactants. In the present study, NO and NO_2 levels only in the range 80-150 ppb were applied (for comparison ISO: 1 ppm) for which first order kinetics are fulfilled.[1] In the optimized photoreactor, uptake coefficients of at least up to ~3×10^{-4} (or photocatalytic deposition velocities of $\nu_{photo} \approx 3$ cm s^{-1}, for definition see ref. [4]) can be determined without significant transport limitation of the reactants to the surface.

The samples were irradiated by a diode array (QUMA-Elektonik & Analytik, Wuppertal), allowing variable UVA irradiance levels between 1-16 W m^{-2} (see Fig. S1 and Fig. S2). The diodes have an intensity maximum λ_{max} = 370 nm ($\Delta\lambda$ ± 20 nm), for which almost all emitted light intensity falls below the threshold limit wavelength for TiO_2 (Anatas) excitation of <388 nm. The irradiance was determined via a small planar cosine correcting optical diffuser (Ocean Optics CC-3-DA) connected to a diode array mini-spectrometer (Ocean Optics USB 4000). The irradiance was averaged over 12 different positions 2 mm behind the Pyrex window (at the same distance as the sample) using only the upper cap of the reactor. The Ocean Optics system was calibrated by intercomparison with a calibrated spectrophotometer with an electronically cooled Charge Coupled Device (CCD) detector (Meteoconsult) for measuring actinic fluxes. For the intercomparison a UV/VIS fluorescence bulb at 1 m distance was used, for which the cosine correction of the Ocean Optics system is near unity and the irradiance is equal to the actinic flux.

S3 Analytical Instrumentation

Nitrogen oxides (NO_x = NO + NO_2) were measured by chemiluminescence detection of NO using a molybdenum converter for NO_2 conversion (Eco-Physics CLD 899Y, detection limit: 25 ppt). The NO_x channel of the instrument shows quantitative interferences against NO_z species ($NO_z = NO_y - NO_x$), thus overestimating the NO_2 level.[6] However, since HONO was found to be the only significant NO_z species formed in the photocatalysis of NO_x on the paint sample,[1] the

NO_2 concentration was simply calculated from the difference of the "NO_2" signal and the measured HONO level (see below). Both channels of the instrument were calibrated by a certified NO calibration mixture (Messer, 450 ppb, stated accuracy of ≤5 %). The converter efficiency for the NO_x channel of unity (100±1 %) was regularly controlled by an O_3 titration unit (Ansyco GPT/00).

HONO was measured by a sensitive and selective LOPAP instrument (Long Path Absorption Photometer), which is explained in detail elsewhere[7,8] and which was successfully validated against the spectroscopic DOAS technique under complex atmospheric and smog chamber conditions.[9] During the laboratory study the instrument had a detection limit of ~5 ppt for a time resolution of 3 min.

The temperature of the paint surface was measured by a calibrated thermocouple (Omega Engineering GmbH, Type K, 0.5 mm diameter, accuracy ±0.5 K), while the relative humidity and the temperature of the reaction mixture behind the reactor were measured by a calibrated humidity sensor (HYTELOG-USB, Hygrosens Instruments GmbH, accuracy ±2% RH). The relative humidity on the sample surface in the photoreactor was calculated based on the absolute humidity, derived from the temperature and relative humidity of the Hygrosens senor and the average temperature of the surface during irradiation, using a simple form of the Clausius Clapeyron relation ($p(H_2O) = 10^{(8.946-2260/T)}$ in [Torr]).

S4 Experimental set-up

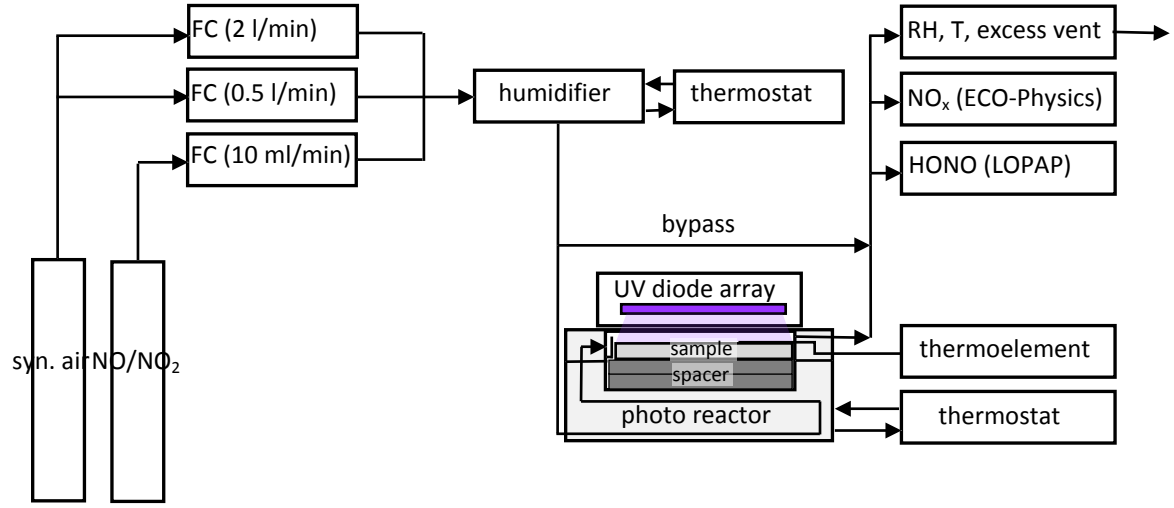

Fig. S2: Experimental set-up (FC: flow controller).

References Supplement

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