Heterogeneous Conversion of Nitrogen Oxides on Commercial Photocatalytic Dispersion Paints

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INTRODUCTION

- NO_x (NO+ NO_2) plays an important role in the atmosphere, controlling O_3 formation and acid deposition.
- NO_2 is a harmful trace gas for which new threshold limit values were implemented in the EU in 2010. These limits (e.g. annual mean: 40 µg/m³) are typically exceeded under urban conditions.
- Photocatalytic degradation of NO_2 on environmental surfaces (paints, concrete, glass, etc.) may help to reduce [NO_2].
- TiO_2 (anatase) is a known photocatalyst for NO_2, e.g. [1-4].
- However, harmful products were identified on pure TiO_2 surfaces:
  - Nitrous acid (HONO), [1, 2]
  - Nitrous oxide (N_2O), [3, 4].

AIM OF THE STUDY

- Kinetic and mechanistic study on heterogeneous reactions of NO_x on commercial photocatalytic dispersion paints.
- Formation of harmful products?
- Estimation of the NO_x reduction under urban conditions.

EXPERIMENTAL

- Commercial photocatalytic dispersion paints (Sto PhotosanNOX)
- Flowtube study under atmospheric (c, r.h., hν) conditions (Fig. 1)
- Actinic flux (<390 nm) similar to the atmosphere (Fig. 2). E.g. $J(NO_2)_{\text{all lamps/with sample}} = 0.008\ s^{-1}$
- NO/NO_2 measured by chemiluminescence/"blue light" converter
- HONO measured by the LOPAP technique
- N_2O by GC/ECD
- Adsorbed nitrite/nitrate by ion chromatography

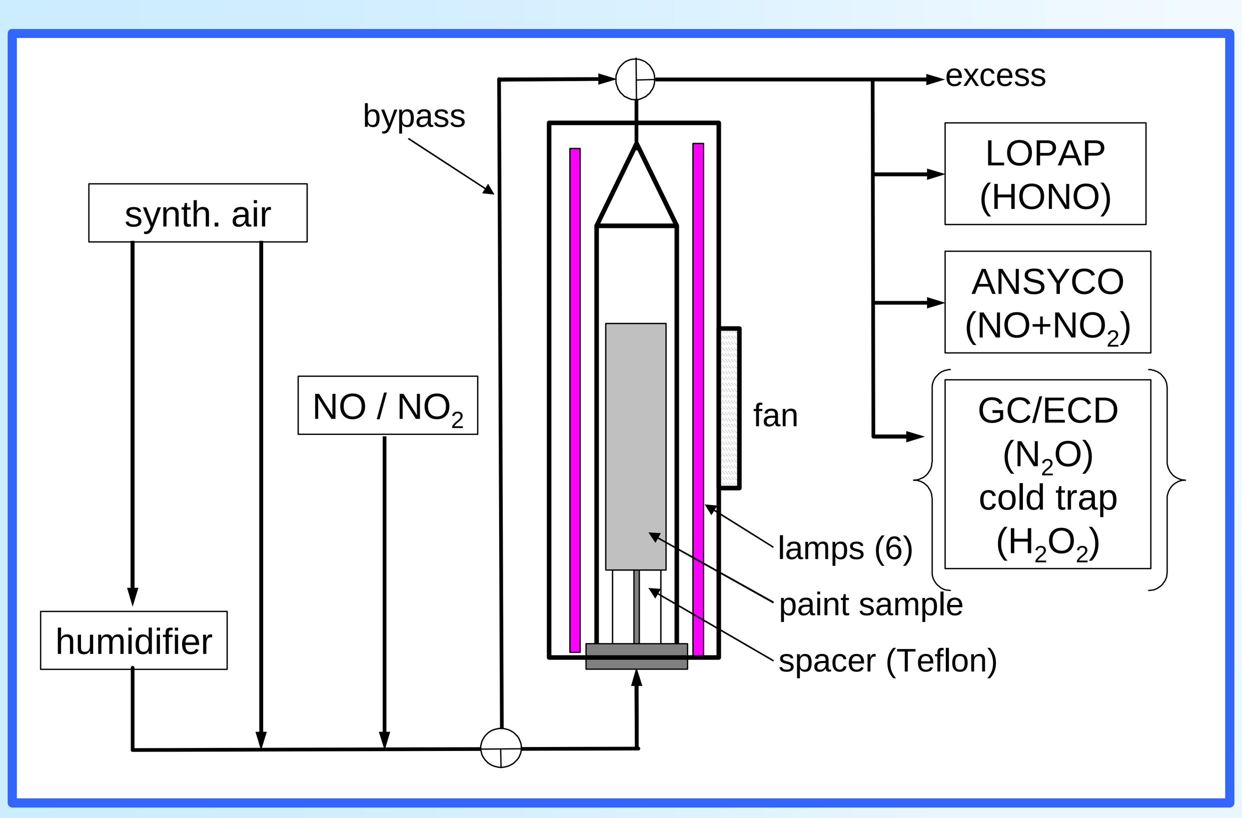

Fig. 1: Experimental set-up

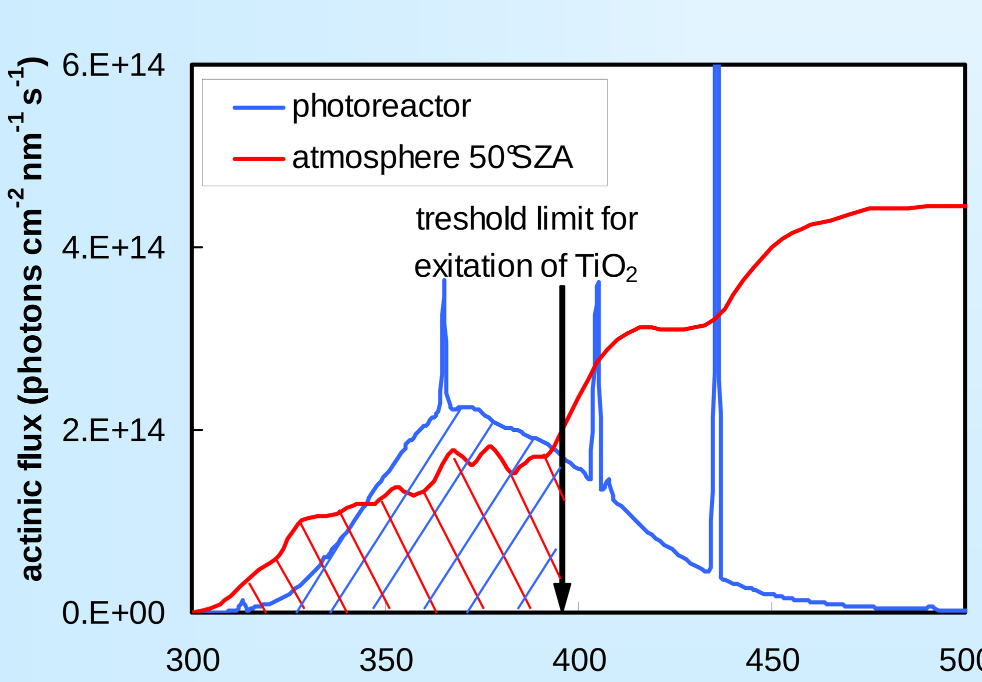

Fig. 2: Actinic flux in the photoreactor compared to the atmosphere

ACKNOWLEDGEMENT

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RESULTS

1. Product study

- Slow dark reaction of NO_2 and heterogeneous formation of HONO both, on photocatalytic and non-catalytic reference paints
- Fast photocatalytic degradation of NO and NO_2 ($\gamma > 10^{-5}$)
- HONO also strongly decompose under irradiation

⇔In contrast to studies on pure TiO_2 surfaces [1, 2]

- Small NO_2 formation in the photocatalytic reaction of NO
- No formation of N_2O
- Quantitative formation of nitrate (yield ca. 90 %)
- Small yield of H_2O_2 only in the presence of O_2

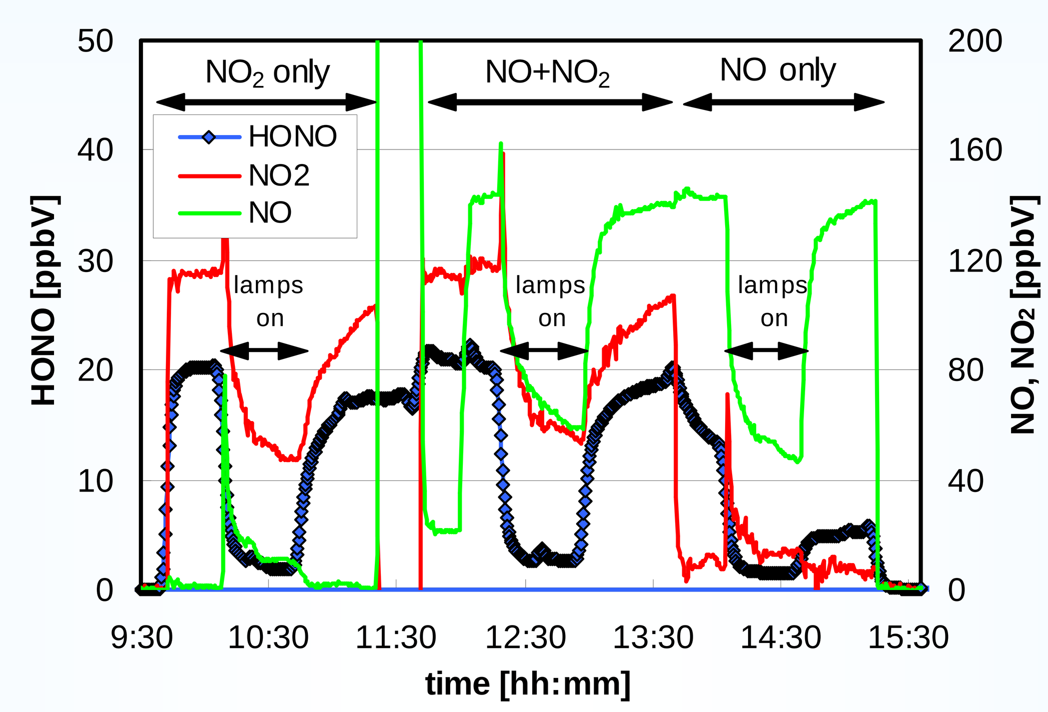

Fig. 3: Photocatalytic degradation of NO_2, NO_2+NO and NO

2. Dependencies

- Rate constants (1. order) were obtained by modelling of the experimental data including the know Leighton chemistry
- $k(NO+TiO_2)$, $k(NO_2+TiO_2)$ independent on the concentrations
- $k(NO+TiO_2)$, $k(NO_2+TiO_2)$ correlate linear with light intensity
- Strong humidity dependence:
  - $k(NO+TiO_2)$ decrease with increasing r.h. ➔ H_2O not necessary
  - $k(NO_2+TiO_2)$ increase first with increasing r.h.➔ H_2O necessary
  - $k(HONO+TiO_2)$ increase with increasing r.h. ➔ H_2O necessary

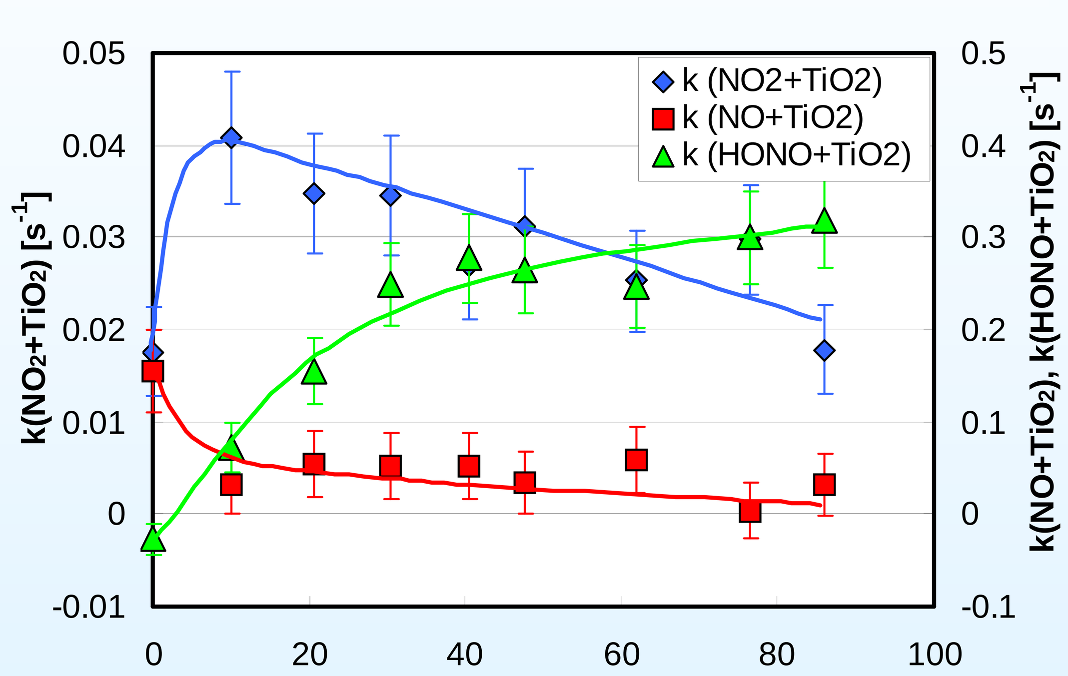

Fig. 4: Humidity dependence of the rate constants of NO, NO_2 and HONO on photocatalytic paints

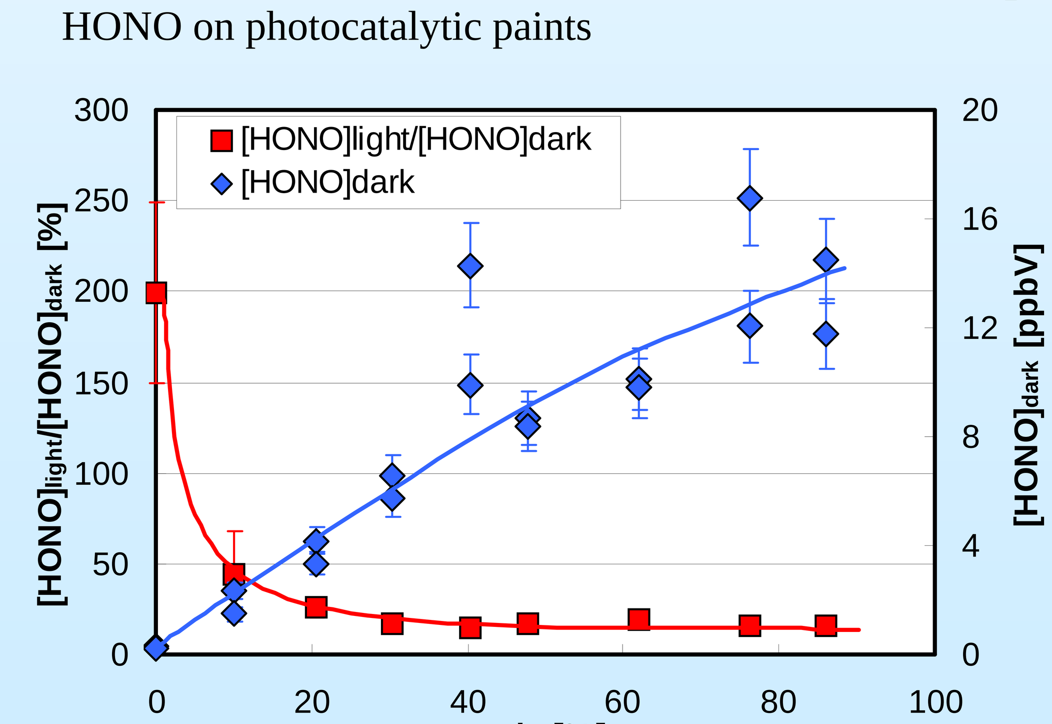

Fig. 5: Humidity dependence of the heterogeneous HONO formation/decomposition in the dark and under irradiation

RESULTS (cont.)

3. Proposed Mechanism

- Photoexcitation of TiO_2 leads to the formation of $e^-(cb)$ and $h^+(vb)$
- $e^-(cb)$ ➔ initiate reduction: $O_2 + e^-(cb) \rightarrow O_2^- \rightarrow \mathbf{HO_2}$
- $h^+(vb)$ ➔ initiate oxidation: $H_2O + h^+(vb) \rightarrow \mathbf{OH} + H^+$
- After both reactions, TiO_2 is in its initial state (➔ catalyst)
- Formed radicals (HO_2/OH) react with adsorbed nitrogen oxides ➔ nitrate (NO_3^-) as final product
- HONO only reacts as nitrite (NO_2^-) in a film of adsorbed water

➔Fast HONO reaction only under alkaline/humid conditions

⇔Can explain differences to other studies on pure TiO_2 [1, 2]

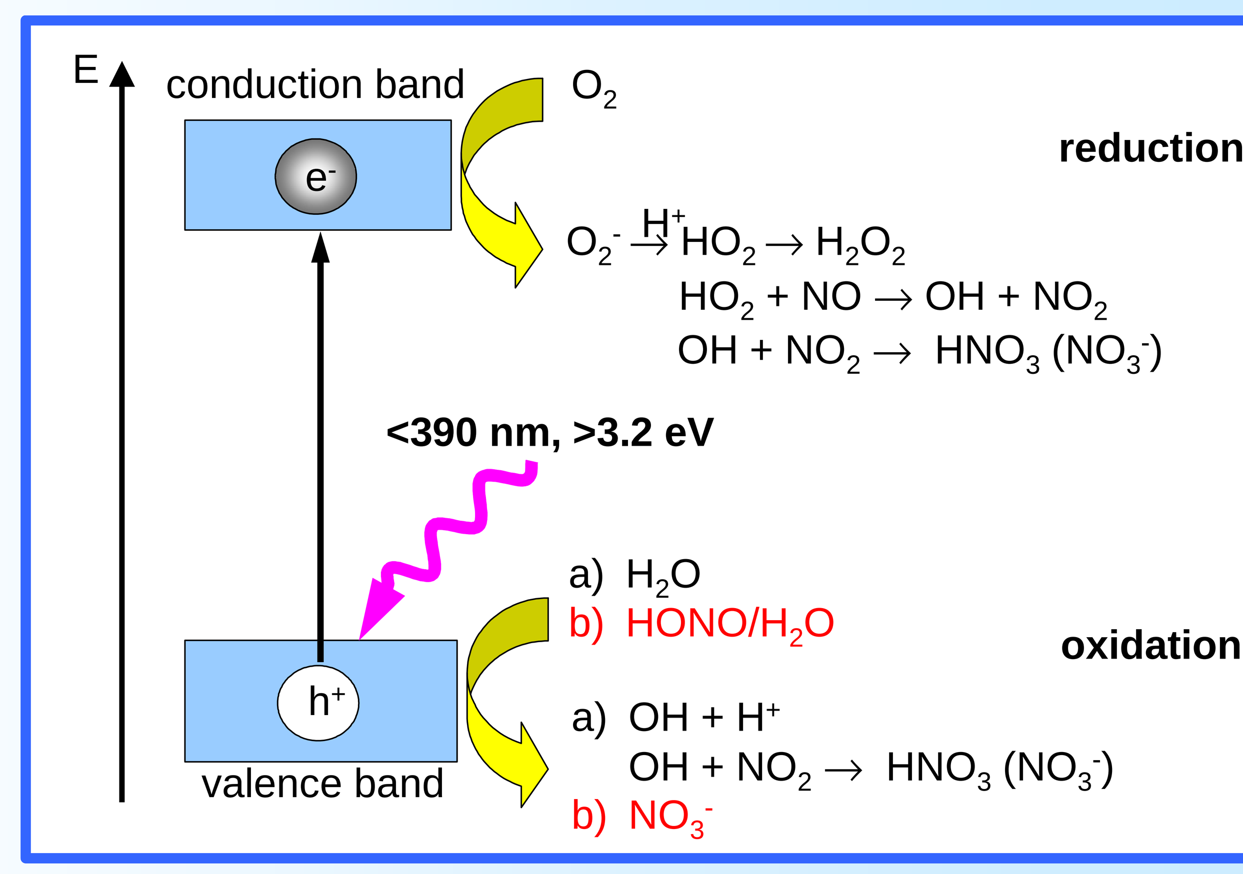

Fig. 5: Proposed mechanism

ATMOSPHERIC IMPLICATION

☺**All harmful nitrogen species studied (NO, NO_2, HONO) strongly decomposed on photocatalytic paints (γ>10⁻⁵)**

☺**No N_2O formed**

➔**Application of photocatalytic paints recommended**

- **Near unity yield of HNO_3/nitrate**

☹**HNO_3/nitrate leads to an acidification and eutrophication of the environment**

➔**But: application recommended, since:**

a) **HNO_3 is formed almost quantitatively from NO_x also in the atmosphere (*day:* NO_2+OH, *night:* NO_2+O_3→→)**

b) **Photocatalytic paints will reduce gas phase HNO_3 and its impact on plants and humans**

- **Recent NO_x reduction in a pilot street canyon (*S/V: 1 m⁻¹*) measured during the PICADA project: *40-80 %***
- **But: k(het) ~ S/V, typical street canyon (20 x 20 m) S/V: *0.1 m⁻¹***

➔**Expected NO_x reduction in a typical street canyon:**

ca. 5-10 %

- **Should be verified ➔ EU-Project: *PhotoPac* (LIFE+)**
- **May help to reach new threshold limit values for NO_2**
- **Almost cost neutral, in contrast to the new "environmental protection areas" in Germany**

REFERENCES

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