Heterogeneous Conversion of Nitrogen Oxides on Commercial Photocatalytic Dispersion Paints

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INTRODUCTION

- NO₂ (NO+ NO₂) plays an important role in the atmosphere, controlling O₃ formation and acid deposition.
- NO₂ 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 on environmental surfaces (paints, concrete, glass, etc.) may help to reduce [NO₂].
- TiO₂ (anatase) is a known photocatalyst for NO₂, e.g. [1-4].
- However, harmful products were identified on pure TiO₂ surfaces:
  - Nitrous acid (HONO) [1-2]
  - Nitrous oxide (N₂O) [1-4]

AIM OF THE STUDY

- Kinetic and mechanistic study on heterogeneous reactions of NO₂ on commercial photocatalytic dispersion paints.
- Formation of harmful products?
- Estimation of the NO₂ reduction under urban conditions.

EXPERIMENTAL

- Commercial photocatalytic dispersion paints (Sto Photosan NOX)
- Flowtube study under atmospheric (c, r.h., h.v.) conditions (Fig. 1)
- Actinic flux (390 nm) similar to the atmospheric (Fig. 2). E.g. NO₂ amount in the gas phase: 10⁻⁶ mol cm⁻³.
- NO/NO₂ measured by chemiluminescence/“blue light” converter
- HONO measured by the LOPAP technique
- N₂O by GC/EC
- Adsorbed nitrite/nitrates by ion chromatography

RESULTS

1. Product study

- Slow dark reaction of NO and heterogeneous formation of HONO on photocatalytic and non-catalytic reference paints
- Fast photocatalytic degradation of NO and NO₂ (h > 10⁻⁸)
- HONO also strongly decompose under irradiation
- In contrast to studies on pure TiO₂ surfaces [1-2]
- Small NO₂ formation in the photocatalytic reaction of NO
- No formation of N₂O
- Quantitative formation of nitrate (yield ca. 90 %)
- Small yield of H₂O₂ only in the presence of O₂

Fig. 3: Photocatalytic degradation of NO₂, NO/NO₂ and NO

2. Dependencies

- Rate constants (1. order) were obtained by modelling of the experimental data including the known Leighton chemistry
- k(NO+TiO₂) ki(ON+TiO₂) independent on the concentrations
- k(ON+TiO₂) ki(ON+TiO₂) correlate linear with light intensity
- Strong humidity dependency:
  - k(ON+TiO₂) decrease with increasing r.h. → H₂O not necessary
  - k(ON+TiO₂) increase with increasing r.h. → H₂O necessary

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

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

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REFERENCES


ATMOSPHERIC IMPLICATION

- All harmful nitrogen species studied (NO, NO₂, HONO) strongly decomposed on photocatalytic paints [1-5]
- NO and NO₂ formed
- Application of photocatalytic paints recommended
- Near unity yield of HONO/nitrate
- HONO/nitrate leads to an acidification and eutrophication of the environment
- But: application recommended, since:
  a) HONO is formed almost quantitatively from NO₂ also in the atmosphere (day): NO₂→OH radical, NO₂→OH (reactions)
  b) Photocatalytic paints will reduce gas phase HONO and its impact on plants and humans
- Recent NO₂ reduction in a pilot street canyon NOI: 1 m² measured in the PICAD project: 40-80 %
- But: k/ν-1/S, typical street canyon (20 x 20 m) S/ν: 0.1 m²
- Expected NO₂ reduction in a typical street canyon: ca. 5-10 %
- Should be verified EU-Projekt: PhotoPac (LIFE+)
- May help to reach new threshold limit values for NO₂
- Almost cost neutral, in contrast to the new "environmental protection areas" in Germany