Improved Photocatalysts for selective NO_x-degradation

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Motivation

The air we breathe is our most important resource. But it is contaminated with many different harmful substances such as ozone, volatile organic compounds (VOCs) or nitrogen oxides (NO_x). The main part of the emissions are generated by anthropogenic sources, *i.e.* human activities. The European Union introduced strict maximum permissible values by the guideline 2008/50/EG to improve the air quality. These were transferred in national law 2010. As a result of these two decrees, different actions taken to achieve the target values, namely low emission zones, forbidden areas for heavy vehicles or more strict emission values for vehicles. However, these measures only had negligible effects on the concentration of NO_x. Especially the maximum annual average value of 40 µg/m³ NO_2 is still frequently exceeded by most German cities. Some sampling stations even register concentrations as high as 80 µg/m³, twice the allowed value. The active reduction of the amount of harmful substances by photocatalysis is a new and promising approach for an improved air quality that could achieve what all the passive actions tried before.

Importance of NO_x

Nitrogen oxides are generated by high temperature processes under air *e.g.* road traffic, industry, air transportation, heating systems. They are primarily responsible for photochemical smog and acid rain.

NO_x describes the sum of both nitric oxide and nitrogen dioxide:

$$NO_x = NO + NO_2$$

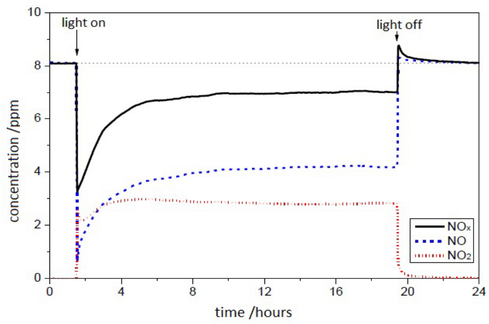
NO: LC_{50} = 854 ppm (rat, 4 hr)[1]

NO_2: LC_{50} = 86 ppm (rat, 4 hr)[2]

NO_2 is much more toxic to humans and animals than NO. Additionally, it is a source of ozone and respirable dust. Consequently, the emission restrictions mainly refer to NO_2 and measures to reduce the pollutant levels should be concentrated on NO_2 rather than the reduction of total NO_x.

State of the Art

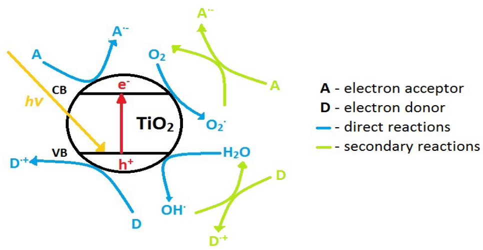
To this day, the quality of photocatalysts is only measured according to their reduction of NO or total NO_x. There is no differentiation between the different species despite their vastly different risk potential.



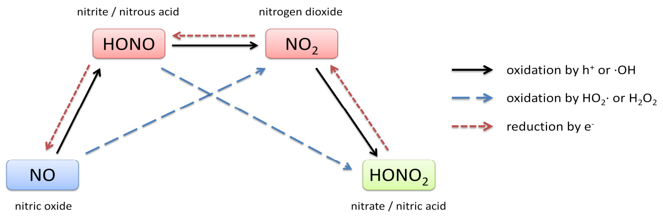
If the NO_2 concentration is measured during a photocatalytic NO oxidation test, it becomes clear that the release of NO_2 is a critical problem. In most cases, only about 30 % of the introduced NO is transformed into nitrate. The rest is just oxidized to NO_2.[3] It is also produced by the catalyst in the case of surface saturation with nitrate. Additionally, the behavior of ozone in combination with photocatalysts is still unclear.

Photocatalysis

Photocatalysis is based on the photon absorbing property of the semiconductor, in this case TiO_2:



In consequence of the photon absorption, one electron is transferred from the valence band (VB) to the higher energy conducting band (CB). If the electron is generated on the surface, it can reduce molecular oxygen to superoxide ($O_2^{\cdot-}$) and hydrogen peroxide (H_2O_2). The related hole in the VB oxidizes water molecules to hydrogen radicals (•OH).

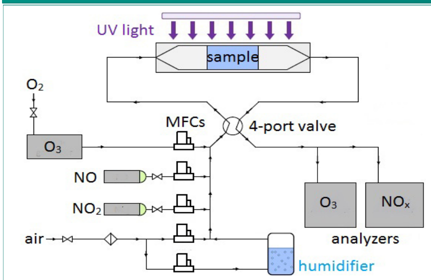


The reactive oxygen species can be used to oxidize NO_x to the harmless nitrate which can be removed from the catalyst surface by rain. To achieve a high selectivity, it is important that the back-reaction (reduction of already formed nitrate) is suppressed. In this project, we will explore the effect of co-catalysts on the back-reaction and consequently the selectivity of the reaction.

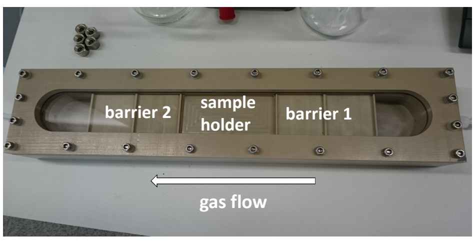
Aims of the Project

1. Titanium dioxide materials will be surface modified with inexpensive co-catalysts of the transition metal group for an improved selectivity to nitrate.
2. The used modification process will be designed by a simple impregnation technique. This enables the use of commercial TiO_2.
3. The influence of ozone in the photocatalytic process will be clarified.

Set-up



The used set-up is based on the ISO norm 22197-1 for photocatalytic degradation of NO and extended to also encompass a NO_2 and ozone source and analyzer. Synthetic air is used as carrier gas which is humidified and enriched with a set concentration of nitrogen oxides and directly synthesized ozone. Typical concentrations also found on real streets with a high traffic will be chosen. The gas mixture will be passed into the reactor with the catalyst which is illuminated by UV light. Inside the reactor, special turbulence barriers will guarantee an optimal mixing. Afterwards, the gas composition change is analyzed.



References

[1] N.G. Ivanov and E. N. Szubaev, *Toksikol Nov. Prom. Khim. Vesh.*, 1979, **15, 53-58**.

[2] E. Gray, B. Le, F. M. Patton, S. B. Goldberg, and E. Kaplan, *AMA Arch. Ind. Hyg. Occup. Med.*, 1954, **10, 418-422**.

[3] J. Z. Bloh, A. Folli, and D. Macphee, *RSC Adv., 2014*, ***4*, 45726-45734.**