DECHEMA FORSCHUNGSINSTITUT

Chemical Technology

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.

State of the Art

Photocatalysis is based on the photon absorbing property of the semiconductor (Fig. 1), 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 or transported to the surface, it can reduce molecular oxygen to superoxide ($O_2^{\cdot-}$) or hydrogen peroxide (H_2O_2). The related hole in the VB oxidizes water molecules to hydrogen radicals (·OH). These reactive oxygen species can be used to oxidize NO_x to the harmless nitrate which can be removed from the catalyst surface by rain.

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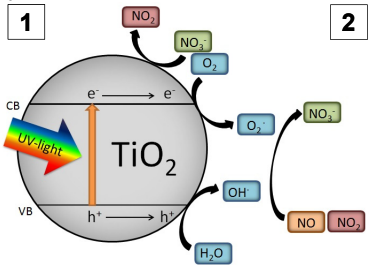

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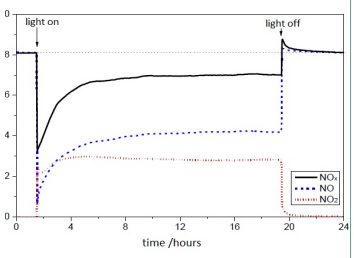

To this day, the quality of photocatalysts is only measured according to their removal of NO or total NO_x. If the NO_2 concentration is measured during a photocatalytic NO oxidation test, it becomes clear that the release of NO_2 is a critical problem (Fig. 2). In most cases, only about 30 % of the introduced NO is transformed into nitrate. [*] The rest is just oxidized to the intermediate NO_2. It is also produced by the catalyst in the case of surface saturation with nitrate .[*]

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

Aims of the Project

In this project, we will explore the effect of transition metal (iron, manganese, copper) oxides as co-catalysts to achieve a higher selectivity and suppress the formation of NO_2. The metal ions were added to the surface of commercial TiO_2 materials by a simple impregnation technique and enable multi electron reactions with molecular oxygen (Fig. 3). These reactions are energetically more attractive (Fig. 4) and consequently suppress the reduction of already formed nitrate. Additionally, the role of ozone in the photocatalytic process will be clarified.

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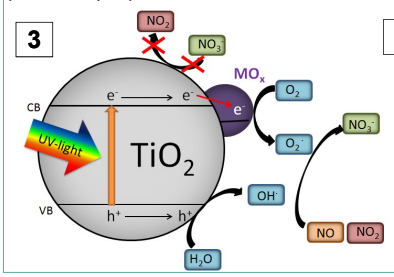

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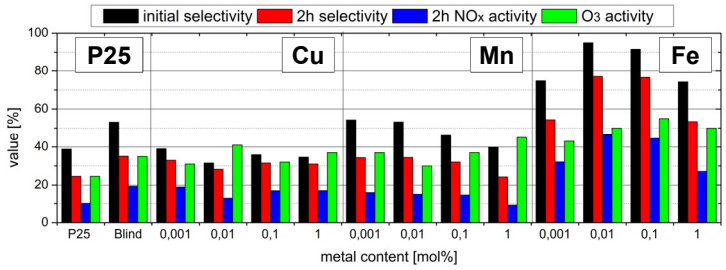
1 electron reaction:
$O_2 + H^+ + e^- \rightarrow HO_2^{\cdot}$
E_0 = -0.05 V vs. RHE

2 electron reaction:
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$
E_0 = +0.68 V vs. RHE

4 electron reaction:
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
E_0 = +1.23 V vs. RHE

Results

The commercial TiO_2 material Aeroxide P25 was modified with different amounts of metal ions and tested for their NO_x and O_3 reduction behavior.



An notable selectivity and activity increase for NO_x degradation of +10% was attained by just "washing" the TiO_2 material (P25 vs. Blind sample) without addition of any metal ions in the process. Even grafting of copper or manganese ions has no further effect. Iron modified materials have considerably higher selectivity and activity compared to the other materials. This effect can be adjusted by choosing the right iron concentration. A metal content of 0.003 to 0.1 mol% iron is the optimum range for Aeroxide P25 .

Comparable trends were found for other commercial TiO_2 materials like Hombikat (Huntsman) or calcined KronoClean K7050 (Kronos). The activity and selectivity for NO_x degradation is only increased by iron addition while the reduction ability of O_3 can be increased by all chosen metals.

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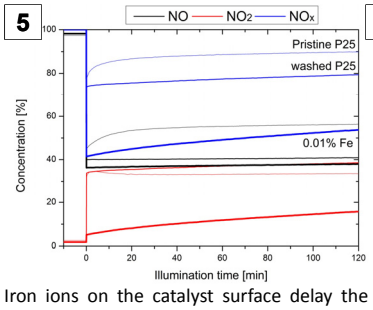

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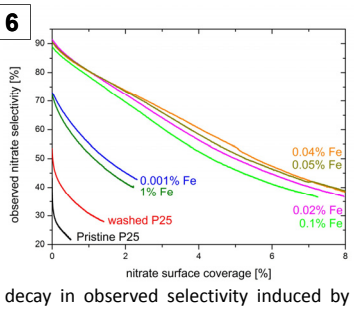
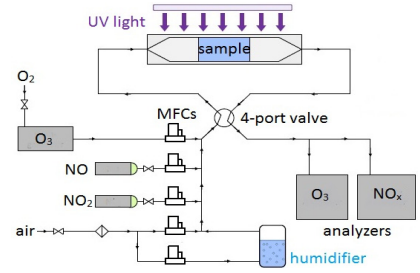


Iron ions on the catalyst surface delay the decay in observed selectivity induced by nitrate accumulation on the surface. (Fig. 5). This effect is related to a higher tolerance towards nitrate poisoning (Fig. 6) and a increased oxygen reduction. Consequently, activity and selectivity are increased over an extended time period.

Outlook

1. An simple figure-of-merit for the quality of a will be created to value different photocatalysts and their ability to reduce NO_x and O_3, also taking into account the formation of NO_2 under real life conditions.
2. The long time stability of impregnated materials is still unknown. This knowledge gap will be filled by long term tests.

Set-up



The used set-up is based on the ISO standard 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 are chosen. The gas mixture is 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 change in gas composition is analyzed.