DECHEMA FORSCHUNGSINSTITUT

Kinetics and Reaction Mechanism of the Highly Efficient and Fast Photocatalytic Reduction of Nitrobenzene in Ethanol

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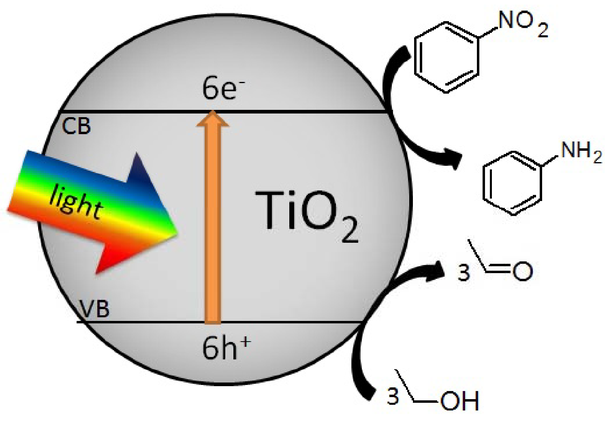
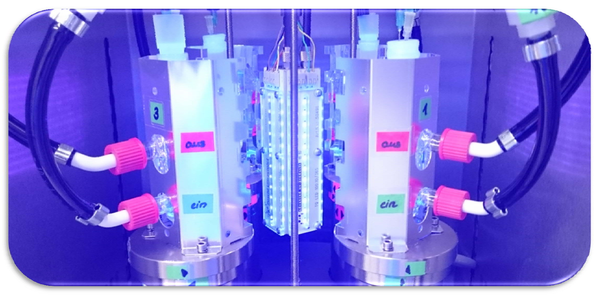
1 Nitrobenzene reduction reaction



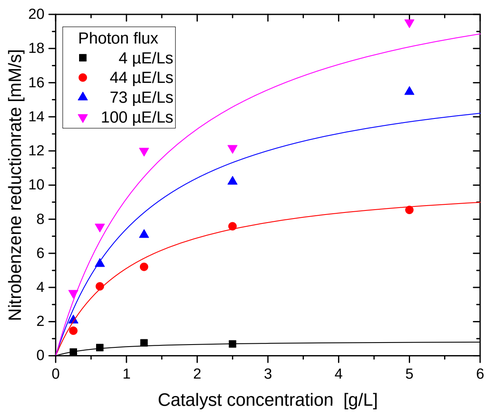
- Electron transfer from the valence band (VB) to the conducting band (CB) by light
- Reduction of one molecule nitrobenzene (NB) to aniline
- Oxidation of 3 ethanol molecules to acetaldehyde
- 6 electrons und holes needed for the whole process
- Under optimal conditions, 10 mM nitrobenzene are fully converted in just 15 minutes

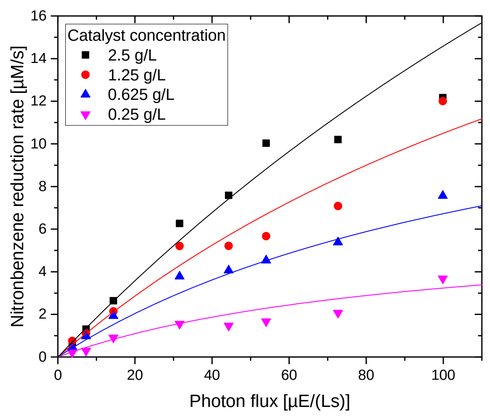
2 Measurements



- photoLAB Batch-S system (Peschl Ultraviolet)
- 365 nm LEDs, 20 ml reaction volume, 25°C
- Ar atmosphere (oxygen free)

3 Light intensity and catalyst concentration



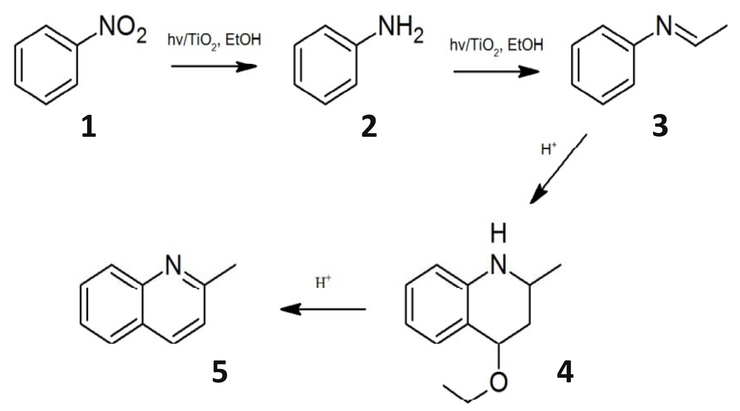


- Increase of nitrobenzene reduction rate with the increase of the catalyst concentration (*c*)
- Saturation behavior at high catalyst loadings
- Point of saturation depends on the photon flux (*I*)
- Nearly linear increase in the reduction rate with increasing photon flux
- The reduction rate (*k*) can be modeled very well using the following equation:

$$k = k_0 I \frac{c}{c + \alpha + \beta I}$$

$k_0 = 0{,}239\ \mu M/s$
$\alpha = 0{,}648\ g/L$
$\beta = 0{,}00948\ gs/\mu E$

4 Subsequent reaction steps to quinaldine



- Condensation of aniline **2** with acetaldehyde to ethylidenaniline **3**
- Condensation is a non-photocatalytic step
- Reaction of ethylidenaniline **3** to 4-ethoxy-1,2,3,4-tetrahydrochinaldin **4** over an unknown pathway, possibly involving ethyl vinyl ether
- 4-ethoxy-1,2,3,4-tetrahydrochinaldin **4** as main product
- Quinaldine **5** not observed as product under chosen conditions

5 Photonic efficiency

$$\xi = \frac{6k}{I}; \xi_{max} = 6k_0 = 143\%$$

- Over 100% photonic efficiency under the assumption of 6 needed photons
- Extremely high efficiency for a heterogeneous photocatalytic reaction (common values < 10%)
- „Current doubling“ could reduce the number of needed photons to 3
- Higher catalyst concentrations are needed at higher light intensities to retain the same photonic efficiency (*ξ*)

6 Summary

- Dependence of nitrobenzene reduction rate on catalyst concentration and light intensity describable with one simple equation
- and (co-)immobilization of the acid catalyst on silica supports

7 Outlook

- Clearing up the reaction mechanism and kinetics of the overall reaction
- Catalyst change from TiO_2 to visible light active materials such as $MgFe_2O_4$ and (co-)immobilization of the acid catalyst on silica supports

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