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Chemical Technology

Photocatalytic Quinoline Production from Nitroaromatic Compounds - QuinoLight -

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Motivation

Photocatalysis with semiconductor nanoparticles can be used in organic synthesis to catalyze reactions such as oxidation and reduction reactions, C-C bond formation or cyclizations. However, despite their many advantages such as high energy input at mild reaction conditions, the use of less energetic substrates and the reduced formation of by-products, photocatalytic reactions are currently of little importance in the chemical industry. The main obstacles for a more widespread use are limited availability of standardized and scalable technical equipment for the reactions and little knowledge of the reaction mechanisms and kinetics which make optimization and scaling up extremely challenging. Furthermore, the photocatalyst and photoreactors are typically not optimized for each other so this has to be done tediously on a case-by-case basis.

In this project, a scalable reactor concept with integrated and harmonized photocatalyst will be developed which will allow heterogeneous photocatalytic reactions to be performed with high efficiency. The photocatalytic synthesis of quinolines directly from nitroaromatic compounds and alcohols will be used as a model reaction.

Concept

Reactor Development

Study of different reactor types with rapid prototyping:

- Batch reactors for slurries
- Continuous reactors for slurries
- Reactors with immobilized catalysts on the surface

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Reaction Engineering

Study of the model reaction in batch reactor system:

- Kinetic studies and modeling
- Optimization of the reaction
- Extension of the product spectrum

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Catalyst design

Development of an visible light sensitive photocatalysts and combination with acid catalyst:

- Synthesis of $MgFe_2O_4$
- Synthesis of the acidic support
- Combination of $MgFe_2O_4$ and acid catalysts

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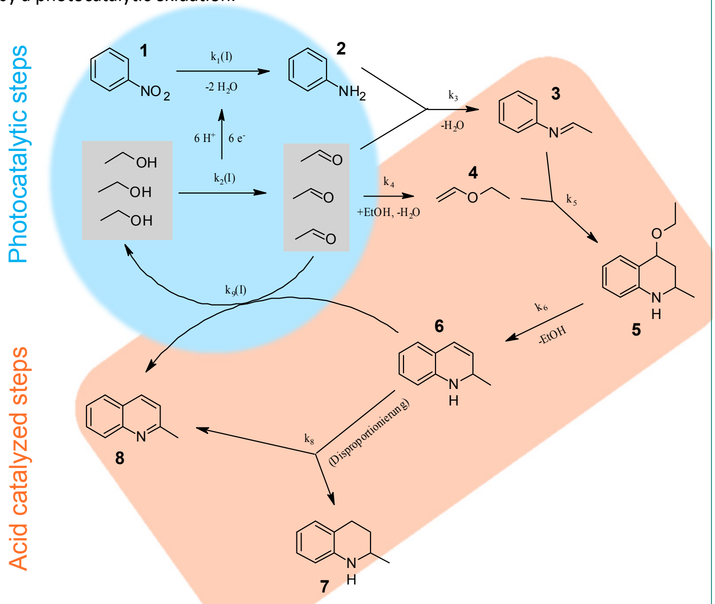
Synthesis of Quinolines

In the first reaction step, nitrobenzene **1** is reduced to aniline **2** and ethanol is oxidized to acetaldehyde by a photocatalytic reaction (blue marked.)Three ethanol molecules and six electrons are needed, respectively. The following steps are acid catalyzed (marked in red). First, aniline **2** is condensed with acetaldehyde to ethylidenaniline **3** which reacts with ethylvinylether **4** to 4-ethoxy-1,2,3,4-tetrahydrochinaldin **5**. The ethylvinylether **4** is formed in an additional condensation with ethanol and an acetal intermediate state. 1,2-Dihydroquinaldine **6** is the result of a elimination reaction of ethanol of **5** which disproportionates to 1,2,3,4-Tetrahydroquinaldine **7** and to quinaldine **8**. Alternatively, 1,2-Dihydroquinaldine **6** can directly react to quinaldine **8** by a photocatalytic oxidation.

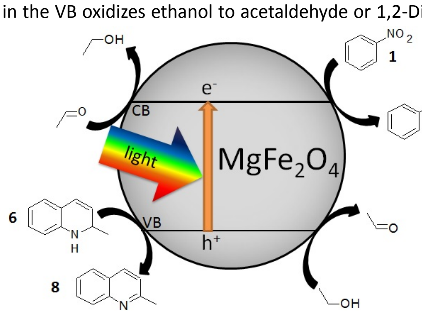


To optimize the synthesis, increase the product amount and the spectrum of products the kinetics of the reaction have to be analyzed and the following questions have to answered:

- Which are the photocatalytic steps and which reactions are influenced by light?
- Influence of light intensity, temperature, amount of catalyst and educts
- Is the reaction rate influenced by the amount of water in the reaction media?
- Can the reaction rate increased by addition of oxidation equivalents?
- Which consecutive reactions are possible under the same conditions?
- It is possible to optimize the quantum efficiency to reduce the energy consumption?
- Which substituents can be introduced at the substrates and which products will be formed?

Photocatalysis

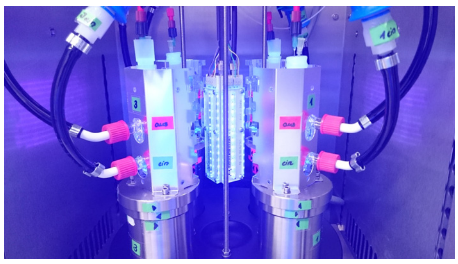
Photocatalysis is based on the photon absorbing property of the semiconductor like TiO_2 or $MgFe_2O_4$: In consequence of the photon absorption, one electron is transferred from the valence band (VB) to the higher energy conducting band (CB). If the electron is generated on or transported to the surface, it can reduce nitrobenzene **1** to aniline **2**. The related hole in the VB oxidizes ethanol to acetaldehyde or 1,2-Dihydroquinaldine **6** to quinaldine **8**.



Most photocatalytical reactions were done with TiO_2 but it needs UVA light for activation. Many organic substances also absorb UVA light which reduces the amount of light for the catalyst and enables secondary reactions. It would be a great advantages to use visible light. Magnesioferrite ($MgFe_2O_4$) has a smaller band gap, adjustable by particle size, and can adsorb green light. The smaller band gap results in a lower oxidation potential of +1.8 V vs. RHE compared to +3.0 V vs. RHE of TiO_2 while the reduction potential is similar.

Set-up

The "photoLAB Batch-S system" from Peschl Ultraviolet is used to investigate the photocatalytic formation of quinolines.



Four equal reactors with a volume of 25 ml are arranged around a 20 W (light flux) lamp with 365 nm LEDs. The temperature of the reaction media and the light intensity can directly adjusted. The reactors are equipped by gas connections to work under oxygen free conditions. The hole set-up is installed in fully closed "photocabinet" to protect the environment from the UV-light.