Plasmonic Catalysed Reactions in a Flow Reactor

with The use of Supported Gold Catalysts under the Influence of Light

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This research was done by the Lumen community

Introduction of the Lumen project

The main goal of project Lumen is to enable the substitution of fossil fuels for sunlight. For this, catalysts that absorb the energy from sunlight as an input for the conversion of starting materials into sustainable products are being researched. [1]

The main question which guided this research was as followed:
Under which conditions can a light activated non-thermal plasmonic active gold catalyst produce the highest yield of a hydrogenation or hydrogenolysis product?

Method of Investigation

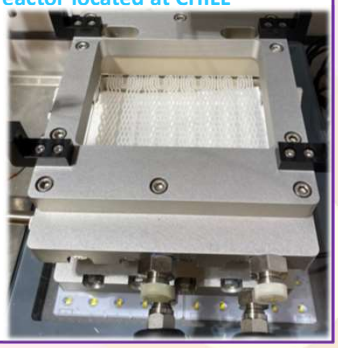
Literature research

When a catalyst under influence of light has a localized surface plasmon resonance effect (LSPR), without the catalyst increasing the temperature due to phonon scattering. It is called a non-thermal effect. This literature research had a focus on finding non-thermal effects in reactions, which produce fine chemicals with the use of a gold catalyst under the influence of light.

Reactions in the hydrogen gas reactor located at CHILL

The reactor is placed on a lamp which simulates sunlight. The sample flows through small channels in the reactor while irradiated. Two reactions had been performed.

Reaction 1 was tested with the first batch of the synthesized $Au@Ru/Al_2O_3$ catalyst. In reaction 3 the activity of a old and a new batch of Au/TiO_2 catalyst got tested.



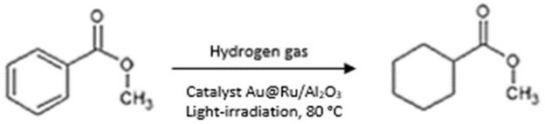
Results and Discussion

Literature research

Theoretically it is (almost) impossible to have non-thermal effects due to the lost energy of the LSPR phonon scattering. Still a lot of papers unintentionally claim to have a solely non-thermal effect in their reactions with the use of a supported gold catalyst under the influence of light. The suspected reason of these false claims is that the actual temperature of the catalyst is hard to measure.

The hydrogenation reaction of methyl benzoate [2] [3]

In the first reaction the reaction time was increased by performing more cycles with less substrate and catalyst in the reaction mixture. The results appeared to be less than 1%.



Methyl benzoate — Methyl cyclohexacarboxylate

Reaction 1. Hydrogenation of methyl benzoate with the use of a $Au@Ru/Al_2O_3$ catalyst.

Table 1. The yield of the hydrogenation reaction of methyl benzoate made with $Au@Ru/Al_2O_3$ as the catalyst.

Volume (mL)		Total Cycles	Yield (%)
Substrate	Catalyst		
50	4	3	0.0
25	2	6	0.3
27	5	9	0.4

Results and Discussion

The synthesis of $Au@Ru/Al_2O_3$ [3]

Because of the low yields obtained with the first hydrogenation reaction with the first batch of the $Au@Ru/Al_2O_3$ catalyst. The focus was placed in optimizing the synthesis of the catalyst.

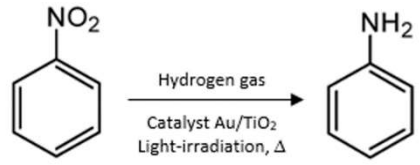
The stability of the nanoparticles are easily affected by parameters as the pH, amount of solvent or materials used. What can lead to the aggregation of the gold particles and so the decrease of reactivity.

Table 1. The average diameter size of the particles in the synthesis 4 steps of the $Au@Ru/Al_2O_3$ catalyst obtained with DLS.

Synthesis Step	Step I	Step II	Step III	Step IV
Average diameter size	130 nm	49 nm	89 nm	2280 nm

The hydrogenolysis reaction of nitrobenzene [4] [5]

The new Au/TiO_2[6] batch of the catalyst had a mistake in the synthesis and the reactivity of this catalyst was tested. The new batch gave significantly lower yield compared to previous reactions with the old batch of the catalyst. Even when the number of cycles got increased for ±3 times the yields were low.



Nitrobenzene — Aniline

Reaction 2. Hydrogenolysis of nitrobenzene with the use of a Au/TiO_2 catalyst.

Table 3. The yield made with the old Au/TiO_2 catalyst batch in the hydrogenolysis reaction of nitrobenzene compared to the new catalyst batch.

Temperature (°C)		Cycles		Yield (%)	
Old	New	Old	New	Old	New
80	80	9	8	4.2	0.4
120	123	9	30	12.6	1.2

Conclusion and Recommendations

Conclusion

- The notation in literature is not optimal in a lot of papers. There are a lot of unintentional claims to have non-thermal effects in reactions, because of not mentioning the thermal effects which could have affected the results.
- It is important to optimize a catalyst synthesis and not to make mistakes, because it will have an impact on the in the activity of the catalyst.

Recommendations

- Optimization of Step IV is recommended.
- New reactions with the further improvement of the $Au@Ru/Al_2O_3$ catalyst and optimize the second reaction with the Au/TiO_2 catalyst without mistakes in the synthesis.

References

[1] Description of *Project Lumen*
[2] Vonk, 2021 | previous student of the Lumen project
[3] de la Garza et al., 2021 | DOI: 10.1021/acsanm.0c03077
[4] Janssen, 2022 | previous student of the Lumen project
[5] Lu et al., 2016 | DOI: 10.1039/C5RA27202E
[6] Martínez Molina et al., 2021 | DOI: 10.1039/C4TA04574B

project LUMEN

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