

Continuous Guerbet reaction of ethanol to butanol using homogeneous MACHO-catalysts

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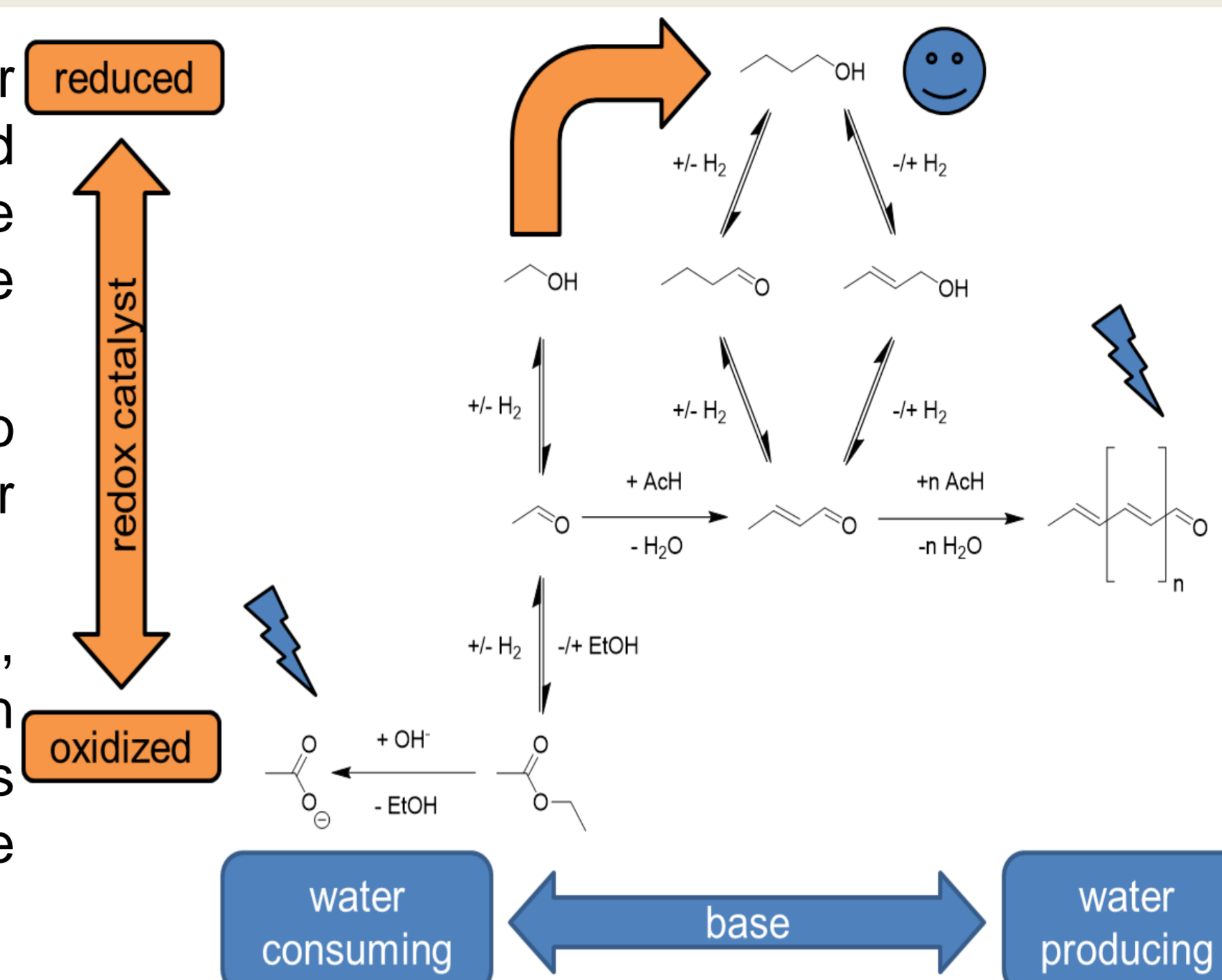
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Introduction

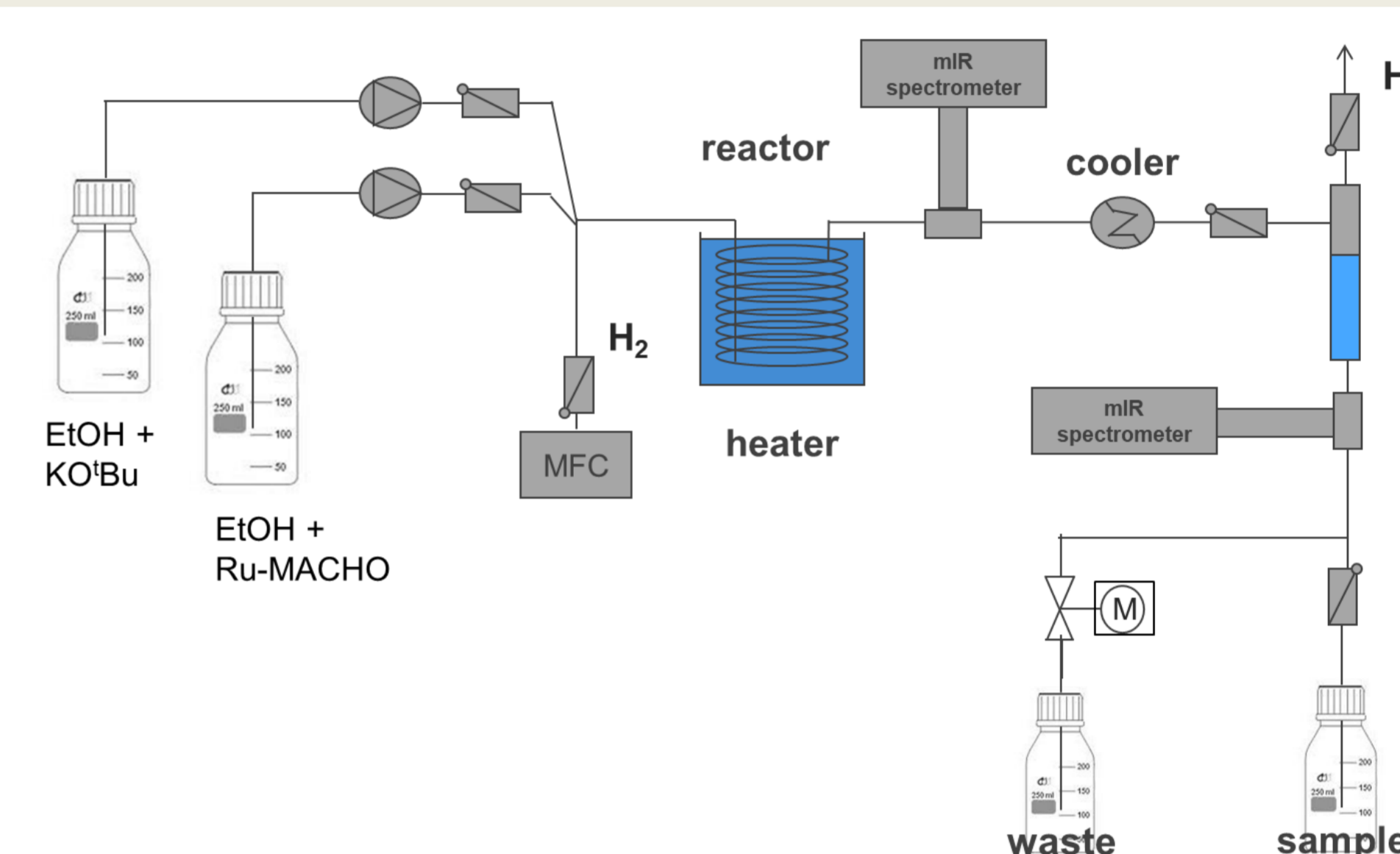
The aim of the Carbon2Chem® project is the utilization of steel mill flue gases as a resource for the synthesis of base and fine chemicals. As part of the SynAlk subproject, CO and CO₂ are used to produce C₂₊-alcohols. [1] On the route to ethanol and higher alcohols, several reactions are carried out in multiphase systems using homogeneous molecular catalysts. In this context the Guerbet reaction is investigated for the direct continuous conversion of ethanol to butanol.

- Ethanol has a lower energy density (70%) than gasoline and it is miscible with water, leading to corrosive influences to current motor engines. Butanol is an ideal drop-in fuel with a higher energy density (90% that of gasoline) and it is immiscible with water → no corrosive effects.
- The Guerbet Reaction, which is known since 1899, is the dream reaction for this conversion, because ethanol could be converted in a one-pot, three-step reaction directly into butanol with only water as byproduct [2]. It works well with a variety of different primary alcohols, but suffers of conversion and selectivity issues when using ethanol as substrate. The formation of acetate (base consumption), higher alcohols or oligomers are main side reactions [3].



Method

- Investigating reaction principles in autoclave-test reactions to determine suitable starting conditions for continuous experiments in a PFTR (plug flow tubular reactor)
- Using Ru- and Mn-MACHO catalysts for the redox steps and KO^tBu as base catalyst
Reaction parameters: 120-170°C; catalyst concentration up to $c_{redox} = 0.5 \mu\text{mol/mL}$, $c_{base} = 1 \text{ mmol/mL}$
- Combining both MACHO catalysts for better performance in the Guerbet reaction
- Determining the conversion rates using ¹H-NMR-spectroscopy
- Determining the gained yields using GC-chromatography



Results

- Ru-MACHO in Guerbet reaction**
 - Very low conversion rates and yields Y in batch experiments ($Y = 7.3 \%$) and continuous experiments ($Y = 3.4 \%$)
 - Fast reaction to butanol ($t < 30 \text{ min}$), but high formation of undesired acetate
 - Formation of 2-BuOH** via rearrangement of the hydroxy group, catalyzed by the Ru-MACHO catalyst
 - Too fast catalysis compared to the relatively slow aldol condensation, leading to a variety of undesired side reactions in continuous experiments
- Combination of both MACHO-catalysts**
 - Using advantages of the slow and selective Mn-MACHO together with the very fast and relatively unselective Ru-MACHO to find a possible sweet spot for the redox equilibria in comparison to the aldol condensation
 - First experiments in a plug flow tubular reactor, showing a beneficial influence when both catalysts are used in the reaction mixture ($Y = 15 \%$) with 1:1 catalyst ratio ($c_{Cat} = 0.5 \mu\text{mol/mL}$ for each catalyst, $c_{base} = 1 \text{ mmol/mL}$)
 - High improvements in the butanol yield by using two redox catalysts with different activities for the (de)hydration in the reaction network
- Mn-MACHO in Guerbet reaction**
 - Mn as an abundant, sustainable earth crust transition metal
 - Better conversion rates and yields in batch experiments ($Y = 19.3 \%$), but with a long reaction time of 8 h
 - Due to the long reaction time, low yields ($Y = 2.2 \%$) after the batch-to-continuous transition in a PFTR
 - Formation of longer alcohols and polymers, because of the low activity of the catalyst in the redox-steps



Conclusion

- Difficult reaction network using ethanol as substrate in the Guerbet reaction shows a variety of different undesired side reactions (formation of higher alcohols/polymers; formation of potassium acetate, which consumes the basic catalyst).
- Ru-MACHO, which is a great redox catalyst, is too active in the catalysis of the (de)hydration steps in the reaction network
 - It is able to produce 2-BuOH in the Guerbet reaction with a rearrangement of the hydroxy group of the unsaturated C₄-alcohol.
- Mn-MACHO is much more selective in the conversion of ethanol to butanol, but requires long reaction times, which is not suitable for batch-to-continuous transition.
- The combination of both redox catalysts seems to be beneficial for the formation of butanol, because the activity in the redox steps can be controlled by the ratio of both catalysts.
- Further investigations via DOE (design of experiment) should search for a catalyst ratio with an ideal reaction rate of the redox reactions compared to the aldol condensation step.

[1] M. Oles, W. Lüke, R. Kleinschmidt, K. Büker, H. J. Weddige, P. Schmöle, R. Achatz, *Chem. Ing. Tech.* **2018**, *90*, 169.

[2] Guerbet, M. C. R. *Acad. Sci. Paris* **1899**, *128*, 1002.

[3] A. Ohligschläger, N. van Staalduinen, C. Cormann, J. Mühlhans, J. Wurm, M. A. Liauw, *Chemistry - Methods* **2021**, *1*, 181.