# Hydrogenation of carbon dioxide to methanol with fluorinated $Cu/ZnO/ZrO_2$-catalysts

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## 1. Introduction

The need to store energy on a larger scale for extended periods of time increases. However, liquid fuels continue to play a very important role in energy storage due to their high energy density, easy handling and storage capabilities[1]. At the same time, the fossil energy consumption and greenhouse gas emissions from usage of current carbon fuels must be reduced drastically[2]. To address these challenges, we use the sustainable electrolysis-hydrogen for the conversion of carbon dioxide to methanol, an easily storable liquid fuel. Our goal is to understand the structure of common copper, zinc, zirconia methanol catalysts treating with diluted fluoric acid. Furthermore the selectivity for methanol and conversion rate for $CO_2$ should be improved[3].

## 2. Experimental

Our methanol catalysts were prepared by co-precipitation from copper, zinc, and zirconia nitrate solutions with sodium carbonate in diluted fluoric acid solution. Different techniques are used for characterization e.g. powder diffraction to prove that the samples are amorphous and free of any byphases. Carbonate and hydroxide groups are analyzable by infra-red spectroscopy. The content of fluorine is achievable by ionic chromatography. Atomic absorption spectroscopy (AAS) for copper/zinc- and dispersive X-ray spectroscopy (EDX) for copper/zinc/zirconia are possibilities to investigate the metal content. To get the optimal calcination and reduction parameters we use thermogravimetric analysis (TGA) and time-programmed reduction and desorption (TPR/D). The catalytic testing is carried out with a 3:1 gas-mixture $CO_2/H_2$ under 40 bar with an average GHSV of ~14000 in our test-rig which was improved over the past four years.

## 3. Results and discussion

The syntheses of the catalyst precursor was investigated and improved during this work. One challenge was avoiding byphases of e.g. sodium zirconia fluorides, which appeared in the first samples. After characterization and calcination we tested the samples in our reactor.

## 4. Conclusion

Further samples are under investigation. First results show a higher selectivity of the fluorinated samples for the methanol reaction.

## References

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