Semester project / Master thesis project

Examination of copper-exchanged offretite for the methane-to-methanol conversion using oxygen looping

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The selective conversion of methane-to-methanol is seen as one of the holy grails of heterogeneous catalysis. This is due to methanol being more readily oxidized than methane, and thereby imposing an unfavorable conversion-selectivity limit on this reaction. Therefore, methanol needs to be protected from subsequent oxidation. One such strategy is the oxygen looping approach, whereby the contact between methanol and the oxidant is avoided. This approach separates the reaction into three distinct stages: i) the (re)activation of the solid catalyst under oxygen; ii) the reaction with the substrate methane, and stabilization of the methyl derivative intermediate; and iii) the desorption of the desired product under steam. One type of material which has been extensively studied in this process are copper-exchanged zeolites. Copper-exchanged zeolites have many benefits in this reaction, such as oxygen being able to be used as an oxidant, which is the only option which is cost-effective.

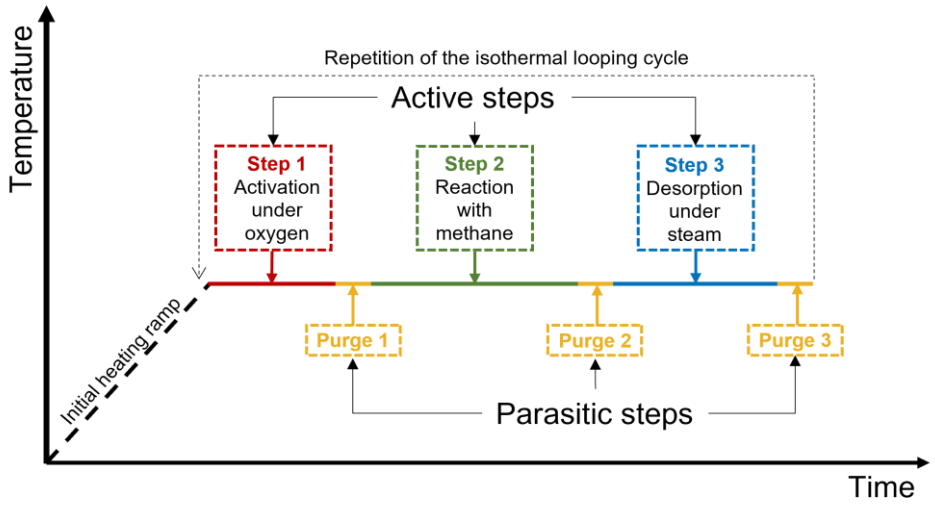

Figure 1: Schematic representation of the isothermal oxygen looping process.

For a methane-to-methanol process to be industrially viable in the case of a gas-solid process, multiple targets have to be met, such as a selectivity above 70 % toward methanol, and a productivity of ~ 3000 µmol $g_{zeolite}^{-1}$ h^{-1}. Increasing these targets is essential for industrial application.

Zeolite offretite (OFF) has a structure very similar to that of zeolite omega (MAZ), which has been shown to be one of the best performing copper-exchanged zeolites for the methane-to-

methanol conversion reaction. Prior unpublished work has shown that zeolite offretite is highly active for the methane-to-methanol reaction. Zeolite offretite has been synthesized in-house with different particle sizes and different copper-loadings. The project is therefore to evaluate the efficacy of copper-exchanged zeolite offretite for the methane-to-methanol conversion, as well as determine the effect of different parameters on the industrial potential of this zeolite.

This project may therefore entail multiple tasks:

1. Characterization of the modified zeolites
2. Construction of a plug-flow reactor system
3. Comparison of different offretite samples in a plug-flow reactor system under different conditions, using mass spectrometry:
    a. What is the effect of different amounts of copper on yield and selectivity
    b. What is the effect of different particle sizes on the yield and selectivity
    c. What parameters (temperature, pressure) produce the highest yield and selectivity

Not all these tasks need to be fulfilled, and the project may be re-tailored to fit different timeframes, as well as the desired practical tasks that wish to be learnt. Depending on the final project, potential learning objectives may be:

1. Training in characterization techniques (sorption measurements, Al-NMR, XRD, etc.)
2. Designing and setting up a reactor system
3. Interpretation of experimental results (Analysis of yields, selectivity, productivity, kinetics)

References

Newton, M. A. *et al*., J. A. Active sites and mechanisms in the direct conversion of methane to methanol using Cu in zeolitic hosts: a critical examination. *Chem. Soc. Rev* **49**, 1449–1486 (2020).

Knorpp, A. J. *et al.* Comparative performance of Cu-zeolites in the isothermal conversion of methane to methanol. *Chemical Communications* **55**, 11794–11797 (2019).

Jovanovic, Z. R. *et al.* Oxidation of methane to methanol over Cu-exchanged zeolites: scientia gratia or paradigm shift in natural gas valorization? *J Catal* **385**, 238–245 (2020).

Knorpp, A. J *et al.* Copper-Exchanged Omega (MAZ) Zeolite: Copper-concentration Dependent Active Sites and its Unprecedented Methane to Methanol Conversion. *ChemCatChem* **10**, 5593–5596 (2018).