

Report for Proposal Code: CH-5378

Proposal Title: Direct methane to methanol conversion on outperforming Cu-MOR catalysts:  
Unraveling Cu-active sites and reaction mechanism by operando XAS

In this experiment we investigated Cu-exchanged zeolites that have been shown to possess Cu-oxo species active towards the direct methane to methanol (DMTM) conversion, carried out through a chemical-looping approach. The direct stepwise transformation of CH<sub>4</sub> to CH<sub>3</sub>OH over Cu-exchanged zeolites has been an intensively researched reaction as it can provide a solution for the utilization of this abundant feedstock. Up to date a commercial process is far from realization, which is why an understanding of the Cu speciation in zeolites as a function of reaction conditions as well as the development of a mechanistic view of the reaction are necessary to further advance the field. In this experiment, we studied Cu-exchanged ferrierite zeolite for the direct CH<sub>4</sub> to CH<sub>3</sub>OH conversion by utilizing X-ray absorption spectroscopy (XAS), in order to assess the local structure and electronic properties of Cu through the reaction. A Cu-FER sample with a Cu/Al = 0.20 and Si/Al = 11 was subjected to three reaction cycles yielding ultimately 96 μmolCH<sub>3</sub>OH/gzeolite. Normalized to the Cu loading, this accounts for 0.33 mol CH<sub>3</sub>OH/molCu, making the sample comparable to very active Cu-MOR materials reported in the literature. During O<sub>2</sub> activation, a transient self-reduction regime of Cu<sup>II</sup> to Cu<sup>I</sup> ions was identified; eventually leading to mostly framework interacting Cu<sup>I</sup> species. CH<sub>4</sub> loading leads to a reduction of these Cu<sup>I</sup> containing species; which are finally partially reoxidized during H<sub>2</sub>O-assisted CH<sub>3</sub>OH extraction. The speciation after CH<sub>4</sub> activation as well as H<sub>2</sub>O-assisted CH<sub>3</sub>OH extraction was assessed via linear combination fitting analysis of the XAS data.

This experiment has resulted in 1 publication and contributed significantly to 1 PhD:

“The impact of reaction conditions and material composition on the stepwise methane to methanol conversion over Cu-MOR: An operando XAS study” Lomachenko, K. A.; Martini, A.; Pappas, D. K.; Negri, C.; Dyballa, M.; Berlier, G.; Bordiga, S.; Lamberti, C.; Olsbye, U.; Svelle, S.; Beato, P.; Borfecchia, E., *Catal. Today* 2019, 336, 99-108.

Dimitrios K. Pappas, “Direct Methane to Methanol Conversion over Cu-Exchanged Zeolites: Building Structure - Activity Relationships” PhD thesis, University of Oslo, 2019