

Proposal Title: Operation induced yield improvement in Cu-zeolite catalysts for the direct methane to methanol conversion: a combined quasi-simultaneous XAS/PXRD study

The global stock of methane from shale gas, hydrates and coalbed methane is constantly increasing but the transportation and processing are challenging. Routes which can transform methane to high value chemicals directly, avoiding the highly energy-consuming syngas route are therefore economically and environmentally desirable. Reactive coupling of methane enables the direct production of olefins and aromatics in a high temperature operation. Direct oxidation of methane needs milder conditions, but suffers from both low conversion and selectivity or involves costly oxidants. Inspired by methanotrophic enzymes with copper in active complexes, it is possible to replicate these sites that are found in nature in the confined environment of zeolite pores. The resulting materials are able to cleave the C-H bond and stabilize a surface methyl-group which is later hydrolyzed into methanol. Until now, different zeolite frameworks (i.e., MFI, MOR, and CHA) have been demonstrated to stabilize Cu in active sites (AS). The direct conversion of methane to methanol (MTM) over these materials involves three consecutive steps: high temperature activation in O<sub>2</sub>, CH<sub>4</sub> loading at 200 °C and finally extraction of the products with steam.

In this experiment, we evaluated Cu-MOR zeolites with diverse different compositional characteristics for the MTM conversion. The normalized product yields per Cu indicate a uniform population of active sites, with the exception of one sample, where the maximum stoichiometry of a di-copper AS – i.e., of almost 0.5 mol activated CH<sub>4</sub>/mol Cu, is almost reached. Aiming to rationalize this unique behavior, we exploited X-ray Absorption Spectroscopy (XAS) to shed light on the nature and dynamics of Cu ions in the MOR zeolite. The subtle differences between active and inactive Cu species formed during O<sub>2</sub>-activation claim call for advanced experimental and analytical approaches, to add species-sensitivity to the absorbing-atom-averaged XAS response. Moreover, the duration of the key reaction steps is observed to largely impact the product yield, demanding requiring the use of consistent reaction conditions for spectroscopy and testing. Having fulfilled these requirements, we unequivocally determined the AS nuclearity as a dimeric site.

This experiment has resulted in three publications and contributed significantly to one PhD:

1. 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., The impact of reaction conditions and material composition on the stepwise methane to methanol conversion over Cu-MOR: An operando XAS study. *Catal. Today* 2019, 336, 99-108.
2. Pappas, D. K.; Martini, A.; Dyballa, M.; Kvande, K.; Teketel, S.; Lomachenko, K. A.; Baran, R.; Glatzel, P.; Arstad, B.; Berlier, G.; Lamberti, C.; Bordiga, S.; Olsbye, U.; Svelle, S.; Beato, P.; Borfecchia, E., The nuclearity of the active site for methane to methanol conversion in Cu-mordenite: a quantitative assessment, *J. Am. Chem. Soc.*, 2018, 140, 15270-15278.
3. Pappas, D. K.; Borfecchia, E.; Lomachenko, K. A.; Lazzarini, A.; Gutterød, E. S.; Dyballa, M.; Martini, A.; Berlier, G.; Bordiga, S.; Lamberti, C.; Arstad, B.; Olsbye, U.; Beato, P.; Svelle, S., Cu-exchanged Ferrierite zeolite for the direct CH<sub>4</sub> to CH<sub>3</sub>OH conversion: Insights on Cu speciation from X-ray absorption spectroscopy. *Top. Catal.* 2019, 62, 712-723.

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