Experiment Report Form

ESRF	**Experiment title:** Exploring activated copper sites for Cu-Omega zeolites with high methane to methanol conversion	**Experiment number**: MA-3679
Beamline: BM26A	**Date of experiment**: from: 13 Septmeber 2017 to: 18 September 2017	**Date of report**: March 5th 2018
Shifts: 15	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*

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Report

Overview

Cu-Omega (MAZ) outperforms Cu-mordenite in the conversion of methane to methanol [1]. However very little is known on the active site or mechanism for the conversion of methane to methanol on Cu-Omega. In this experiment, we attempted to carry out an *in-situ* study of a series of Cu-Omega samples with increasing amounts of copper. The experiment initially had difficulties with isothermality due to heating with a one sided hot air blower. Nevertheless, several samples were measured successfully and provided us with insight in the mechanism of methane to methanol conversion on Cu-Omega. Our preliminary results show that it is a two-electron transfer mechanism between Cu(II) and Cu(I).

Results

BM26A allowed for high quality XANES spectra where we were able to track the copper in-situ for the stepwise conversion of methane to methanol. Figure 1 shows the XANES spectra for the activation and reaction steps. The copper dehydrates during the activation but remains as Cu(II). Once methane is introduced into the system, a large shoulder appears at 8983 which is indicative of Cu(I). The inactive and active samples exhibit very different conversion of Cu(II) to Cu(I). With the inactive omega only converting <5% to Cu(I) while sample with high activity converted 41% of the Copper. This gave us insight in the mechanism for the conversion of methane to methanol. Preliminary result based on the highest copper loaded

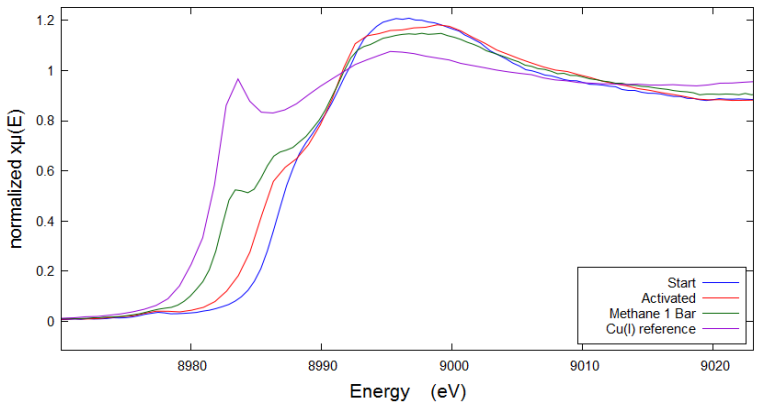

Figure 1: XANES spectra of high copper loaded omega sample

sample show that two Cu(I) are formed per methanol. Further work will be need to be on the complete set of copper loaded omega to validated and see if this applies across the different copper loadings.
EXAFS spectra of the inactive and active Cu-Omega do not have a discriminable difference for k-space up to 12. Unfortunately, higher quality of EXAFS with higher k-space is needed to isolate the active and inactive phases of copper in Cu-omega.

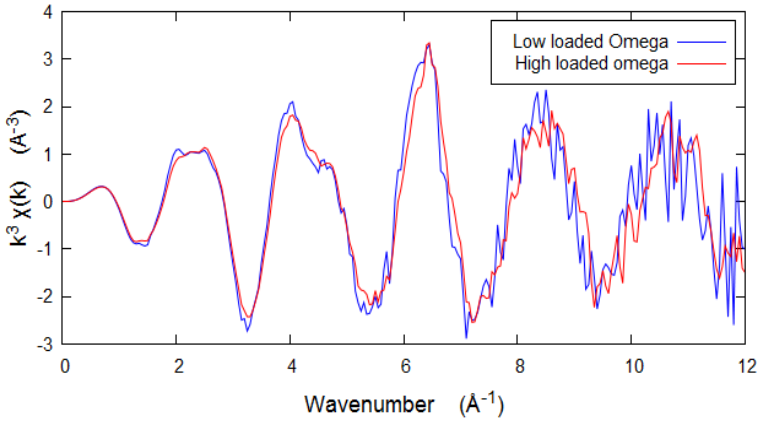

Figure 2: EXAFS spectra of active and inactive Cu-omega

Experimental set-up

The stepwise procedure for conversion of methane to methanol first calls for activation at 450 ºC and then reaction at 200 ºC.For this beamtime we used a hot air blower to heat the sample capillary. We notice high varibility in our results and we investigated this further to understand where and why this variability was coming from (Figure 3).

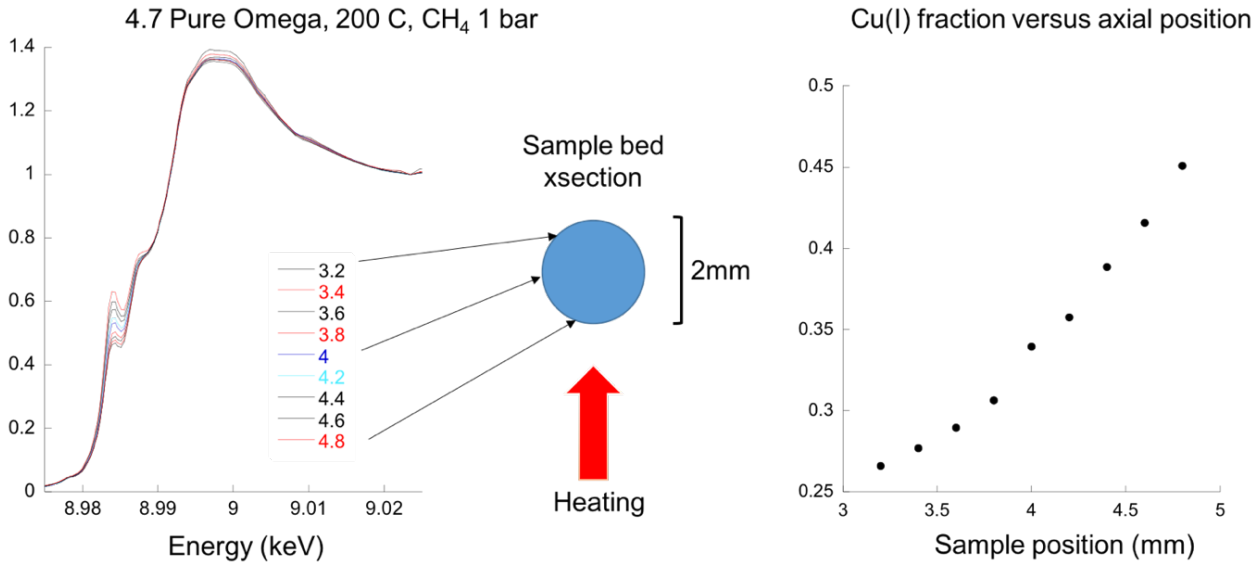

Figure 3: Evaluation of the isothermality across the verticle direction of the capillary

A one sided hot air blower (beamline providde or self-brought) doesn't suffice for consistant and reliable results. This has prompted us to build a double sided heating element for further beamtimes.

[1] Park, M.; Ahn S.; Mansouri A.; Ranocchiari M.; van Bokhoven, J. A. *Chem. Cat. Chem.* ***2017,*** 9, 3705.