Experiment Report Form

ESRF	**Experiment title:** Exploring the low temperature activated copper sites for methane to methanol conversion	**Experiment number**: 31-01-42
Beamline: BM31	**Date of experiment**: from: 09 February 2017 to: 12 February 2017	**Date of report**: March 5th 2018
Shifts: 9	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report

Overview

In this experiment, we compared the conventional high temperature activation procedure to the isothermal procedure for direct conversion of methane to methanol on Cu-mordenite. By using in-situ Cu-K edge XAS at BM 31, we tracked the copper oxidation state during the activation and reaction as pressure was increased to 15 bars. The activation step of the isothermal procedure differs primarly from the high temperature activation in the extent of dehydration. For the isothermal procedure, we were able to successfully measure the reaction at 15 bar methane and found that the Cu(I) conversion increased as pressure increased. By tracking this increase in Cu(I) and comparing it to the increase in reactivity, we gain insight into the mechanism which is is reduction-oxidation.

Results

In figure 1 we compare XANES spectra for the two procedures during the activation stage and confirm that at

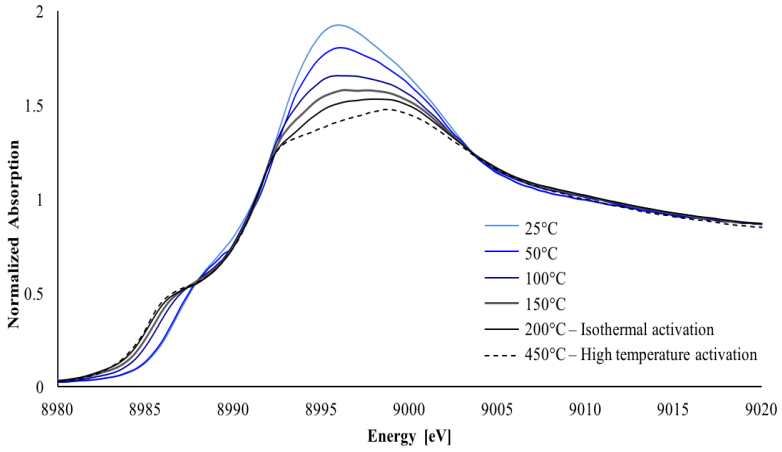

Figure 1: XANES spectra of activation step in the conversion of methane to methanol

the end of the activation step, the isothermal and high temperature activation procedures differ in the maximum absorption which can be indicative of the extent of dehydration. This is interesting observation since most of the proposed active sites like the dimer are believed to be come inactive even at low moisture content[1].

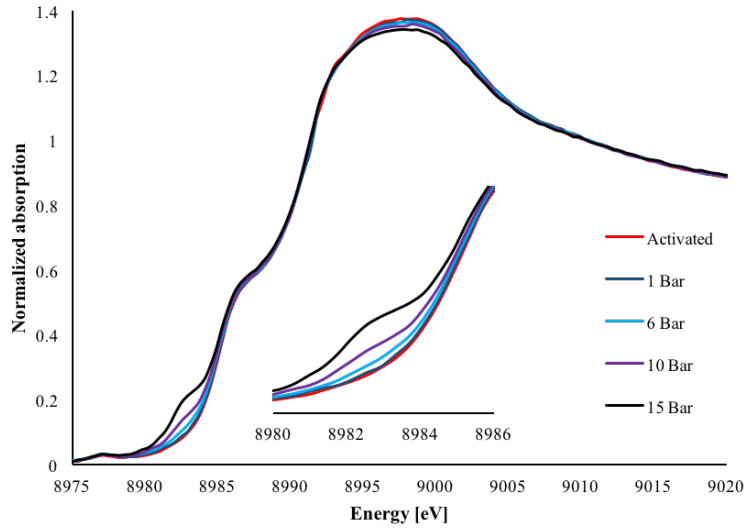

Figure 2: XANES spectra during reaction as methane pressure increased.

During the reaction step, the pressure was increased. We observed an increase in the conversion of the Cu(II) to Cu(I) as pressure increases. Similarly as pressure increases the conversion of methane to methanol also increases.

EXAFS was measure and we obtained high quality of EXAFS. However. The difference between the different pressure show only a small changes. Analysis of the EXAFS to establish the effect of pressure on the active site is on going.

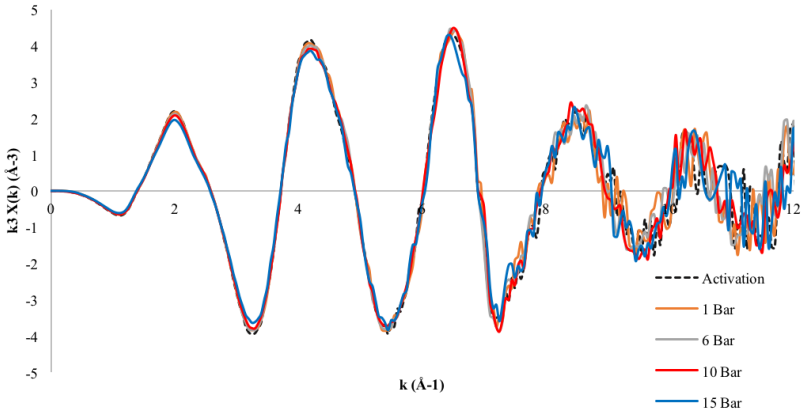

Figure 3: EXAFS spectra as methane pressure is increased.

[1] Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A. Selective Oxidation of Methane by the Bis (U-Oxo) Dicopper Core Stabilized on ZSM-5 and Mordenite Zeolites. *J. Am. Chem. Soc.* **2005**, *127*, 1394–1395