Beamtime report for: **Proposal 31-01-125 (BM31)**

Title: ***From fundamental reaction mechanistics to process-relevant kinetics and durability: effects of desilication in Cu/MAZ on the selective oxidation of methanol***

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Shifts used: 15

Results expected from this proposal

From these studies, we shall be able to quantify the dynamic behavior of progressively desilicated Cu/MAZ for selective methane conversion to methanol and from the viewpoints of both copper speciation (XANES), overall integrity of the material (XRD) and productivity (MS). From such a combined approach, for which BM31 is ideally adapted, we may then rigorously assess, from both fundamental and process related points of view, whether such materials are realistic candidates for application and able to address any of the limiting criteria that currently stand in the way of the use of copper-containing zeolites for this highly sought after conversion.

Results achieved from this proposal.

In effect, we somewhat underestimated the time required to investigate the reactive parameter space required to be studied and therefore did not progress to the use of desilicated and/or mesoporous systems.

However, with the allocated beamtime, and the excellent beamline support, we have obtained sufficient data from an unmodified Cu/MAZ sample, which must be investigated to provide the quantitative basis to understanding how desilication might influence reactive behaviour, to map out the reactive parameter space (pressure, temperature, kinetics) required to assess the performance and overall productivity achievable using this system. These complex datasets, derived from a set of complex chemical processes is, at the time of writing this report, undergoing analysis.

An example of the behavior investigated is given in ***Figure 1***. It can be see that, from the application of time-resolved XAS, we have been able to measure and quantify aspects of copper speciation (oxidation state, degree of hydration, and the kinetics of each of the involved processes) with a high level of precision. When allied to quantitative reactivity (MS) data, a very complete of description of the selective oxidation of methane to methanol using Cu/MAZ will arise. Moreover, we have been able to achieve this for a range of process relevant pressures (up to 10 bar).

As such, although we were unable to move onto studying the effects of desilication on the kinetics and speciation involved, this was a very successful beamtime from which much new information regarding this material and the selective oxidation process will be obtained.

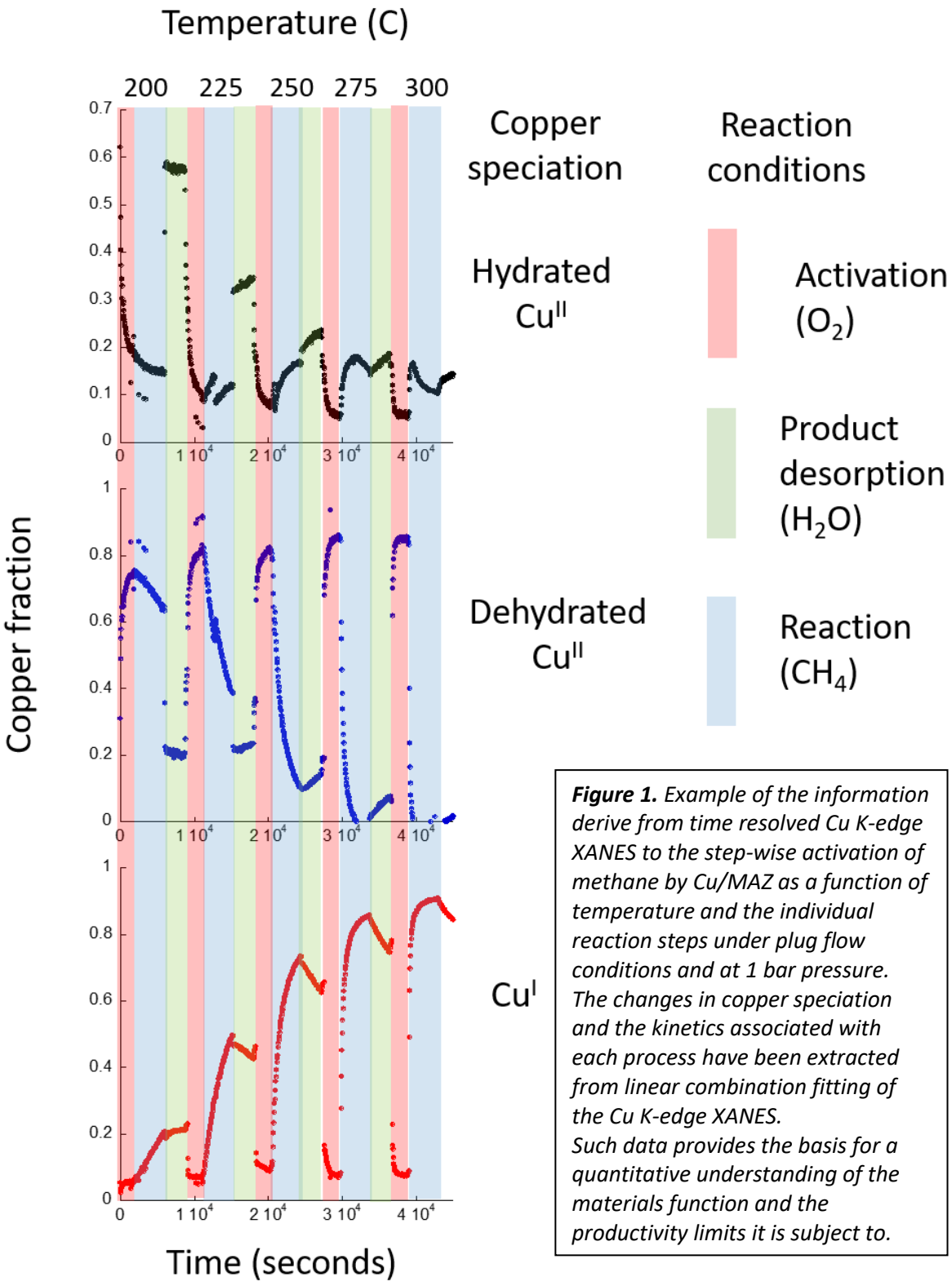

Figure 1. *Example of the information derive from time resolved Cu K-edge XANES to the step-wise activation of methane by Cu/MAZ as a function of temperature and the individual reaction steps under plug flow conditions and at 1 bar pressure. The changes in copper speciation and the kinetics associated with each process have been extracted from linear combination fitting of the Cu K-edge XANES. Such data provides the basis for a quantitative understanding of the materials function and the productivity limits it is subject to.*