

	Experiment title: In situ studies of the structural/electronic changes in catalyst Cu-mordenite during the high pressure oxidation of methane to methanol	Experiment number: HC3050
Beamline:	Date of experiment: from: 26/04/2017 to: 02/05/2017	Date of report: 04/03/2020
Shifts:	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
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Report:

This experiment originally was to conduct powder diffraction at ID22 and X-ray absorption at BM31. Only the shifts allotted at BM31 were scheduled. The experiment carried out at BM31 were focused on in-situ XAS at the copper K-edge through the stepwise conversion of methane to methanol over copper-exchanged zeolites.

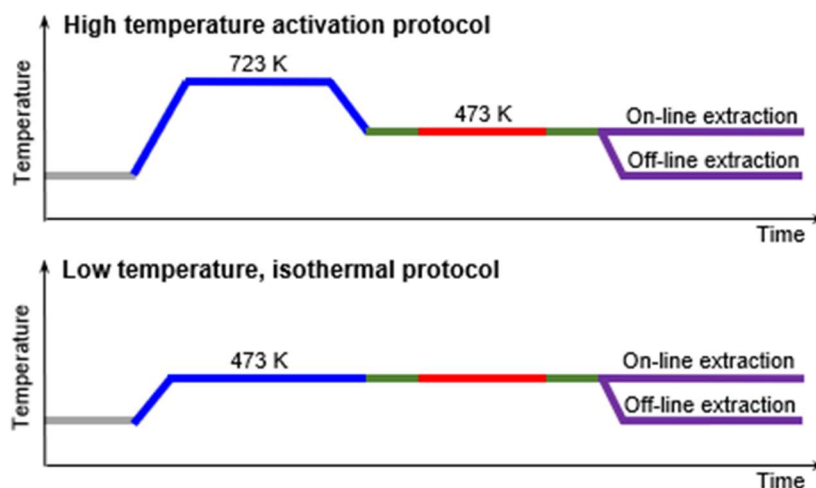


Figure 1: Scheme for low-temperature isothermal and high temperature activation procedures.

Whilst the beamline performed very well and the data of excellent quality it was noted that, we were observing non-uniform heating by the hot airblower especially at higher temperatures. Therefore, we switched to focusing on low-temperature experiments with high pressure and temperature programmed reductions.

We are currently building evidence that the formation of Cu(I) during reaction is indicative of methane reaction, so we followed how quickly the reaction takes place by the Cu(I) formation. We compared two different procedures for the conversion of methane to methanol.

By comparing the two procedures in figure 1, we observed that the isothermal procedure is much slower in reaction. For the high-temperature activation procedure, this reaction takes place quickly, with the vast majority of the active sites converting to Cu(I) by 1500 s as shown in Figure 2. Under isothermal conditions (473 K) with three and six bar methane, this leads to a slow growth of Cu(I), as shown in Figure 2. After 1 h, the reactor cell was pressurized to 6 bar methane, which slightly accelerated the rate of increase of Cu(I).

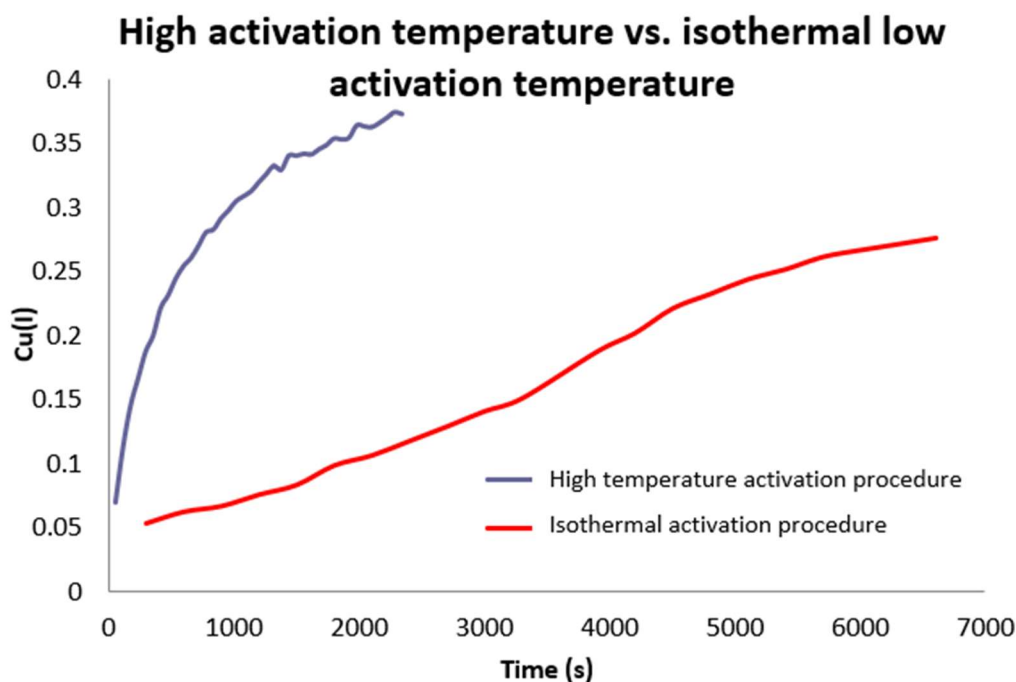


Figure 2: Copper (I) content during reaction with methane under the two different procedures.

This step, therefore takes a considerable amount of time and the most significant barrier in improve the cycle time. The reason for the isothermal being so much slower than the high temperature activation may in part be due incomplete dehydration resulting in possible poisoning of active site and in transport issues.