



	<b>Experiment title:</b> Fundamental insights into the sites for methane activation on Mo/H-ZSM-5: combined XRD and HERFD/XES/Selective XAS studies in operando conditions	<b>Experiment number:</b> CH-3669
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from:22/01/13 to:29/01/13	<b>Date of report:</b> 15/08/13
<b>Shifts:</b> 21	<b>Local contact(s):</b> Mauro Rovezzi	<i>Received at ESRF:</i>
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## Report:

The non-oxidative methane dehydroaromatization (MDA) reaction on Mo/H-ZSM-5 zeolite catalysts is a promising catalytic route for the direct conversion of methane into aromatics. During the so-called induction period of the MDA reaction, the sites responsible of methane activation are formed (either  $\text{MoC}_x$  or  $\text{MoC}_x\text{O}_y$  species), accompanied by partial regeneration of the Brønsted acid sites of the zeolite and the formation of carbonaceous deposits. In order to determine the nature of the  $\text{MoC}_x/\text{MoC}_x\text{O}_y$  species, we combined in this beamtime high resolution fluorescence detection (HERFD) measurements at the Mo K-edge with  $\text{K}\beta$  X-ray Emission Spectroscopy (XES) experiments, studying as well by XRD the possible deactivation of the catalyst due to either framework dealumination or build-up of carbonaceous deposits. Experiments were combined with MS for product gas analysis.

Figures 1a and 1b show the time-resolved Mo K-edge HERFD XANES and XES results. The XANES spectra of the fresh catalyst resembled that for crystalline  $\text{MoO}_3$ , with octahedral coordination. Calcination at  $677^\circ\text{C}$  led however, to gradual edge shift, along with an increase in the pre-edge peak intensity, indicating a different coordination for Mo species. It is known that during calcination the  $\text{MoO}_3$  crystallites migrate into the zeolite channels, forming new Mo species in cation exchange positions. According to the XANES data, these Mo species are tetrahedrally-coordinated. Changes in the absorption edge were also found during the MDA reaction, carried out for 75 min. During the first 10 min, reduction and carburization of Mo was observed, evidenced by a shift in the edge features to lower energies. After 10 min, the spectra look very similar to the spectrum of a  $\text{Mo}_2\text{C}$  reference, remaining unaltered during the course of the reaction.

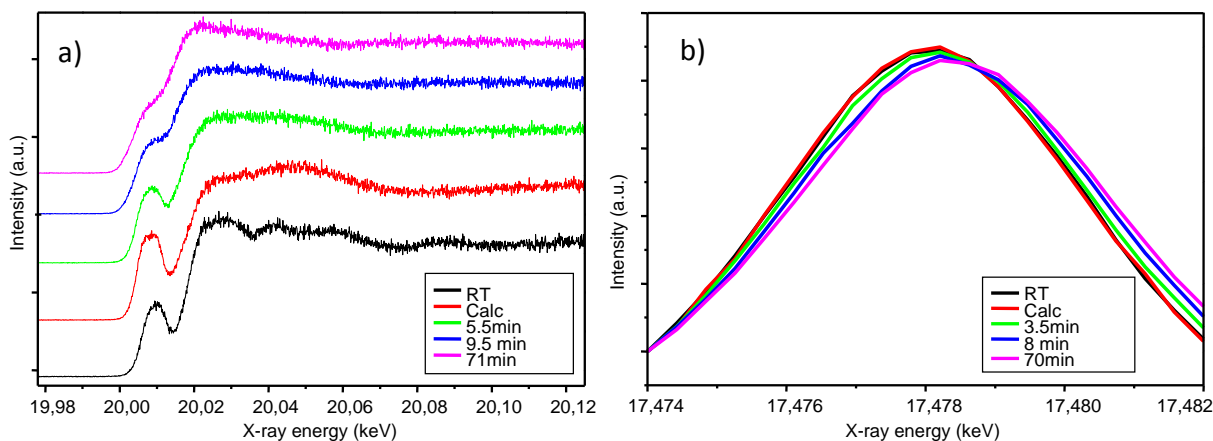


Figure 1. Mo K-edge XANES (a) and XES (b) spectra of Mo-ZSM-5 (4 wt%) zeolite before and after calcination at 677 °C for 2h (20% O<sub>2</sub> in He), and during MDA reaction at 677 °C for 75 min (CH<sub>4</sub>/Ar =1). Just selected reaction times are presented.

The XRD results (data not shown) showed no peak shift or broadening, while a decrease in peak intensity was observed due to beam decay (as confirmed by ex situ measurements of the samples before and after reaction). Hence, both framework dealumination and build-up of carbonaceous deposits can be ruled out as a possible reason of catalyst deactivation during the early stages of the reaction.

To obtain better resolved HERFD spectra, experiments were also carried out quenching the MDA reaction at different times (4, 9 and 75 min). These times were chosen making use of the time-resolved data, according to the most important spectroscopic events observed.

Complementarily, we also performed site selective XAS to determine the nature of the coordinating oxygen species within the ZSM-5 zeolite and their importance for activity. The experiments were also performed quenching the MDA reaction (4 and 25 min). As depicted in Figure 2, the spectrum acquired after 25 min of reaction shows the disappearance of the K<sub>β</sub>'' emission band, typical of oxides, together with a shift to lower energies of the K<sub>β</sub>4 band, as observed in the spectrum of a Mo<sub>2</sub>C reference.

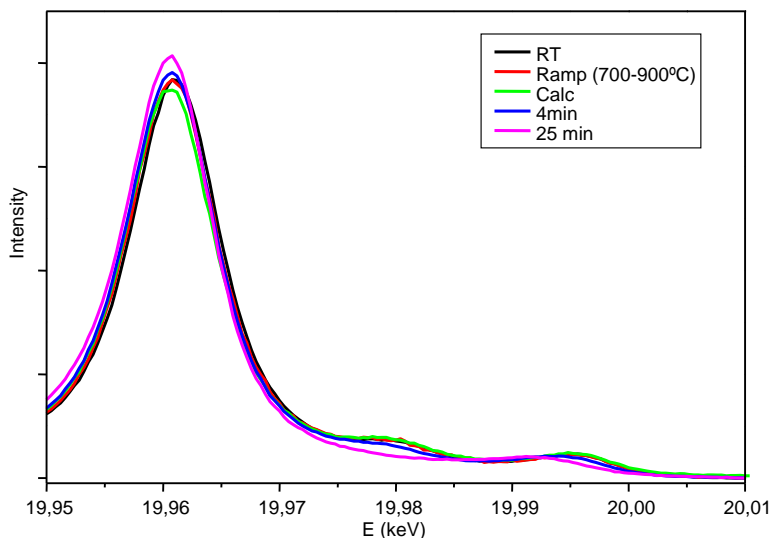


Figure 2. Site selective XES spectra of Mo-ZSM-5 (4 wt%) zeolite before and after calcination at 677 °C for 2h (20% O<sub>2</sub> in He), and after 4 and 25 min of the MDA reaction at 677 °C.

Calculations using FEFF and ORCA packages are currently under way to link the spectroscopic signature to the Mo chemical environment. These simulations should provide a better insight into the type of Mo formed during the induction period of the MDA reaction.