Enabling effective characterization of Mo_2C for the aromatization of methane- Is CO carburization, a non-coking alternative towards Mo_2C, equivalent to CH_4 carburization?

The session at the BM26B DUBBLE from the 6th to the 7th of April 2017 was very successful. No difficulties were encountered during the experiment and all planned samples were measured. Following the suggestion of Alessandro Longo, the 311 crystal was used, which lead to very high resolution spectra, especially in the pre-edge region (Figure 1). The results were used in a recent publication: Vollmer, I., et al. (2018). "On the dynamic nature of Mo sites for methane dehydroaromatization." Chemical Science. XANES spectra were measured ex-situ at the Mo K-edge in transmission. Those measurements on pelletized samples provide XANES spectra with a very signal to noise ratio. Prior to measurement, the fresh samples were dehydrated under a flow of N_2 at 400 °C for 16 h. CO carburization was performed on a custom-made setup, where a 30 ml/min flow of 2.5% CO in He was continuously fed to the reactor. Effluent gasses were analyzed by a quadrupole mass spectrometer (Balzers) connected on-line with the reactor. Mass Spectra were recorded in multiple ion detection (MID) mode using a channeltron detector. Quantification of CO and CO_2 was achieved by calibrating signals with calcium oxalate.[2] Signals were normalized with the signal of He and the fragmentation contribution of CO_2 $m/z = 44$ was subtracted from $m/z = 28$. The catalyst was pretreated at 350 °C in He overnight to desorb any adsorbed gasses from the pores of the zeolite. Carburized samples were transferred from the carburization setup to the glovebox without exposure to the atmosphere, where they were packed into custom-made holders under inert atmosphere. Figure 2 shows the readouts on the MS during CO carburization at different temperatures. These quasi in-situ results are shown in Figures 3-4 for the 2MoHZ-13 and 5MoHZ-13 catalysts. The results confirm a similar carburization state of Mo species obtained by CH_4 pulsing or CO pre-treatment. Thus the answer to the question set out in the title can be answered positively. This knowledge will also be used for a future publication, were the same CO-treatment is used to prepare samples for characterization with CO FTIR and ^{13}C MAS NMR. These experiments helped determine the oxidation state of Mo and three different kind of species were identified to be present on the catalyst. For details please refer to the publication mentioned above.

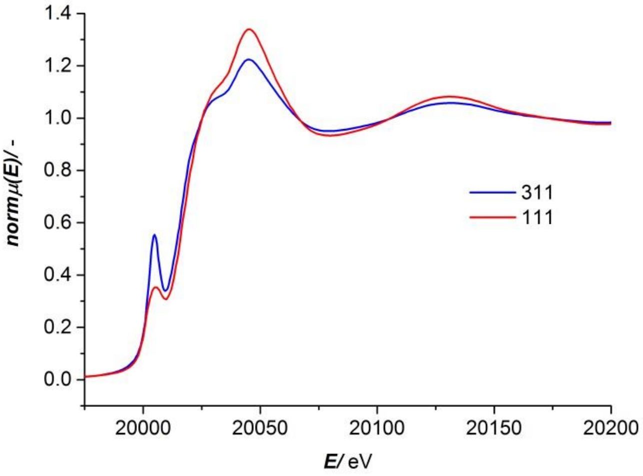

Figure 1: XANES spectra of $Al_2(MoO_4)_3$ *measured with the 311 crystal and measured in a previous beamtime (26-01 1077) with the 111 crystal.*

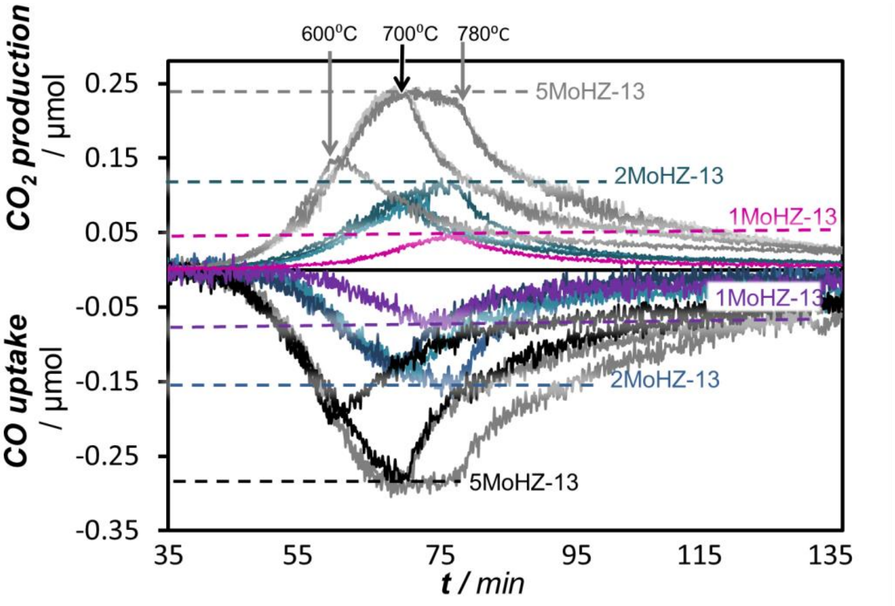

Figure 2: CO_2 *evolution (positive scale) and CO consumption (negative scale) upon CO carburization of 2 wt.% and 5 wt.% Mo on HZ-13 with 30 ml/min 2.5% CO in He at 600 °C, 700 °C and 780 °C. Line colors correspond with the sample colors, maximum temperatures applied for the carburization are indicated with arrows at the top.*

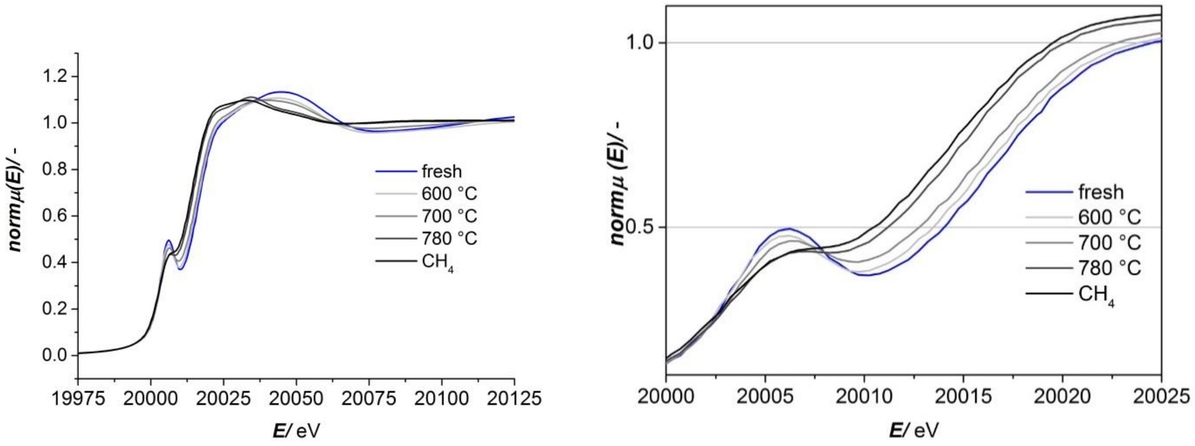

Figure 3: XANES spectra of 2MoHZ-13 collected at Mo K-edge carburized at 600, 700 and 780 ^{0}C as described in section "CO carburization" compared to a sample taken from the reaction with methane, which was quenched right at the onset of benzene formation (indicated as "CH$_4$") and a sample degassed at 400 ^{0}C. All samples were transferred to the glovebox after treatment, where they were packed into XAS sample holders. The right graph presents a zoom-in of the edge.

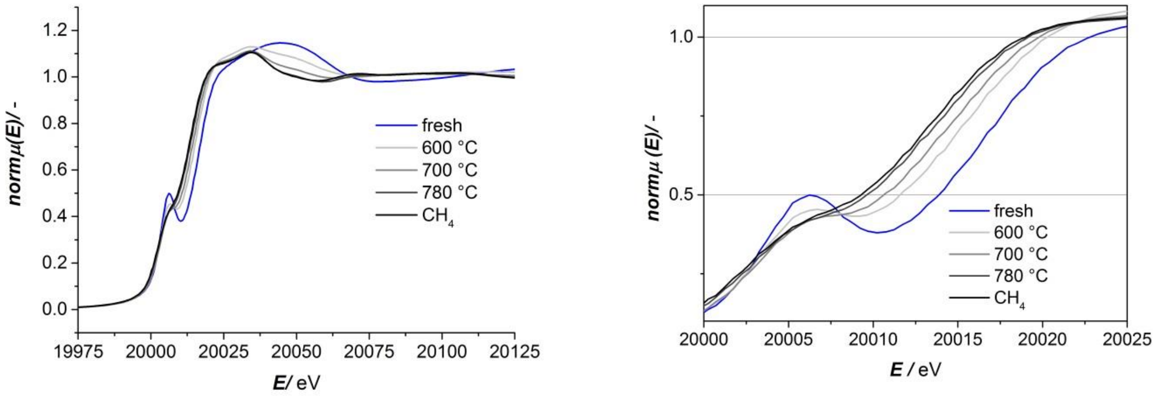

Figure 4: XANES spectra of 5MoHZ-13 collected at Mo K-edge carburized at 600, 700 and 780 ^{0}C as described in section "CO carburization" compared to a sample taken from the reaction with methane, which was quenched right at the onset of benzene formation (indicated as "CH$_4$") and a sample degassed at 400 ^{0}C. All samples were transferred to the glovebox after treatment, where they were packed into XAS sample holders. The right graph presents a zoom-in of the edge.