	Experiment title: Understanding Hydrocarbon Formation and Catalyst Deactivation on Zeolite Catalysts by In-Situ X-ray Raman Spectroscopy	**Experiment number**: CH-4405
Beamline: ID20	**Date of experiment**: from: 17/06/2015 to: 23/06/2015	**Date of report**:
Shifts: 18	**Local contact(s)**: Christoph Sahle	*Received at ESRF:*

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Report:

Zeolite deactivation is one of the main concerns on zeolite catalysis as this undesired process results in a decrease in catalytic activity and catalyst lifetime. Two independent mechanisms are generally the source of zeolite catalyst deactivation: the first is the irreversibly loss of active sites by removal of Al from the zeolite framework, whereas the second involves the formation of carbonaceous deposits (coke) during the catalytic reaction hindering the access to the zeolite particle and therefore to the active sites. The reaction and deactivation mechanisms have predominantly been studied only under ex-situ conditions, whilst it has already been well established that relevant insight into the dynamics of the active sites and deactivating species should be obtained under in-situ/real working conditions.

Our CH-4405 experiment was mainly devoted to investigate the formation of carbonaceous species on zeolites under relevant reaction conditions with X-ray Raman spectroscopy (XRS). We collected high resolution K-edge spectra of carbon in a time- and spatially-resolved manner. The catalytic process under investigation was the methanol-to-hydrocarbons (MTH) reaction, an emergent technology to convert any source of carbon into valuable olefins and gasoline range hydrocarbons.

We have performed the experiments by using a designed and constructed experimental setup, consisting of a tubular quartz reactor (1 mm Ø) heated by an in house IR oven. The reactor was connected to N_2 and O_2 gas lines and methanol was introduced in the reactor by a glass saturator. During the MTO measurements, the reaction products were analyzed by mass spectrometry and the the hydrocarbons formed inside of the zeolite were also monitored in-situ by UV-Vis spectroscopy. The experiments were performed in a wide range of temperatures (300-450 °C) with a satisfactory temperature control (± 5 °C).

The beam was focused on a 400(H)x150(V) μm^2 spot and was monochromatized with a double-crystal Si(111) monochromator followed by a Si(311) channelcut. The measurements were performed utilizing the ID20 72-element multianalyzer spectrometer. Spectra were gathered scanning the incident energy while analyzing the scattered radiation using the Si(660) reflection near backscattering, giving an elastic energy

E0=9.68 keV and energy resolution of 0.5 eV (FWHM). X-ray diffraction was also recorded by using a Pilatus CCD camera.

In the first part of the experiment we focused on the distribution of the zeolite catalyst pellets along the catalyst bed. Figure 1 shows the 2D imaging of the catalyst bed by looking at the Compton (top) and elastic (bottom) scattered light. The images show that the zeolite grains are homogeneously-packed between quartz wool.

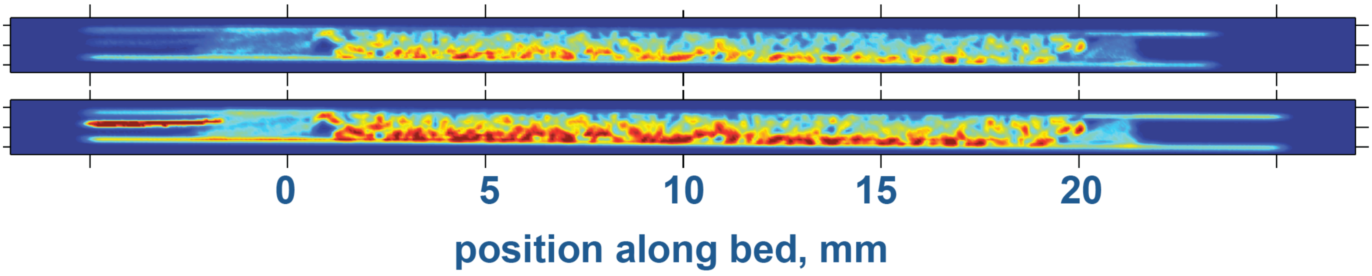

Figure 1. Zeolite distribution along the catalyst bed by looking at the Compton scattering light (top) and the elastic-scattering line.

After imaging the catalyst bed, we aim to understand the deposition of carbonaceous species along the catalyst bed under reaction conditions. To this purpose, we performed an MTH reaction and examine the formation of carbon species along the bed with XRS by looking at the carbon K-edge. We discriminate between the active and deactivated bed zones by looking at the evolution of carbon formation. In this way, the deactivated zones show a high carbon content and this does not change with time onstream. In contrast, the active zones present a lower coke content, which increases with time onstream. The formation of carbon species along the catalyst bed is represented in Figure 2a. These resutls clearly show that the coke front moves from the reactor entrance to the outlet until the catalyst bed is completely deactivated. These measurements were combined with the analysis of the reaction product by MS, which confirms that the reaction bed is completely deactivated when fully coked. Then, the chemistry of the carbon species formed on the active and deactivated zones was studied in detail, Figure 2b shows representative spectras of both zones in-situ. Both carbon K-edges show a strong pre-edge feature at around 285 eV, which is ascribed to the transitions from the carbon 1s to the unoccupied C=C π^* states. The active front shows a more pronounced contribution around 288 eV, which can be due to 1s → 3p σ^* transitions from carbon species with a higher amount of aliphatic C-H functional groups. The measurement performed in this experiment are, to our best knowledge, the first time that carbon species during the MTH reaction are monitor on a catalyst bed with time, space and chemical sensitivity. We are currently analyzing in more detail and planning to submit for publication in the upcoming months.

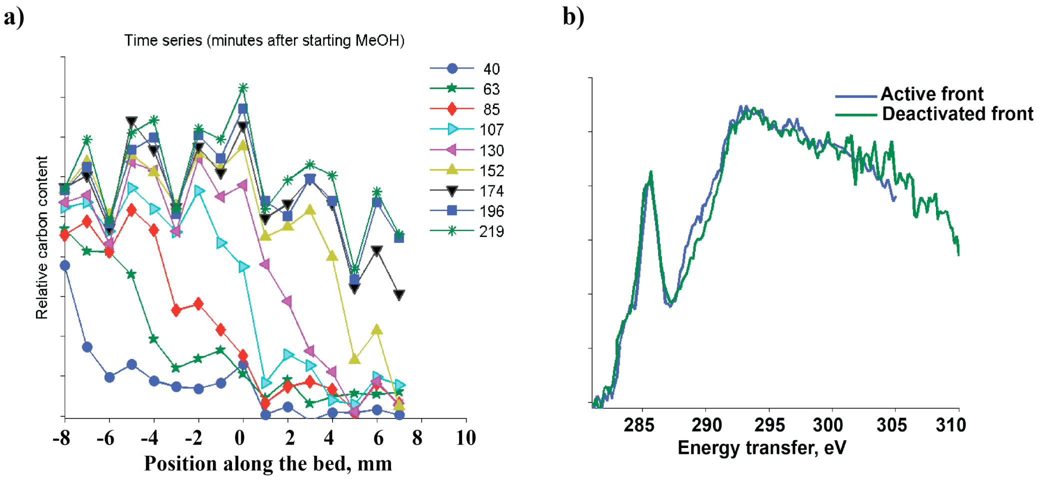

Figure 2. a) Coke distribution along the catalyst bed at different time onstream during the methanol-to-hydrocarbons reaction over an H-ZSM-5 zeolite catalyst. The coke formation was measured by integration of the carbon pre-edge at each point. b) Carbon K-edge representative spectra of the active and deactivated catalyst zone.