



Experiment title: Unravelling the Deactivation Mechanism of Zeolite Catalysts by In-situ X-ray Raman Spectroscopy

Experiment number:
CH-4041

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Report:

The application of zeolites as catalysts in chemical reactions is currently exploited for a wide range of industrial processes. One of the main limitation of zeolites for catalytic application is deactivation, which is the loss in catalytic performance, ultimately resulting in a reduction in catalyst lifetime. Deactivation in zeolites normally include two independent mechanisms: 1) removal of Al from the zeolite framework and therefore modification of the corresponding catalytic acid sites; and 2) formation of carbonaceous species hindering the access to the active sites and the internal structure of the material.

Experiment CH4041 was devoted to the investigation of these two processes with X-ray Raman Scattering (XRS) by an in-situ systematic high resolution study of the L and K edges of Al and the K edge of carbon. Two different processes were studied: first the dealumination process during steaming condition and second the methanol-to-olefins (MTO) reaction.

To address this topic we have designed and constructed an experimental setup, consisting of a tubular quartz reactor (1 mm Ø) heated by an in house IR oven. The reactor was connected to N₂ and O₂ gas lines, steam and methanol were introduced in the reactor by a syringe pump and a saturator, respectively. During the steaming measurements, XRD patterns of the zeolite sample were subsequently collected. For the methanol-to-olefins process, 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 (100-450 °C) with a satisfactory temperature control (± 5 °C).

The beam, which was focused on 400(H)x150(V) μm^2 spot was monochromatized with a double-crystal Si(111) monochromator followed by a Si(311) channelcut.

The measurements were performed utilizing the 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 $E_0=9.68$ keV and energy resolution of 0.5 eV (FWHM).

Diffraction was been recorded with 2θ -scanning pin-diode to probe the structural evolution across the reaction.

In the first part of the experiment we focused on the measurement of the Al L- and K-edges for the reference samples. We used α -alumina as a reference for octahedral aluminum and berlinite for tetrahedral aluminum. Then we moved to the in-situ monitoring of the steaming process of a zeolite H-Y catalyst with a Si/Al ratio of 5, with all the aluminum tetrahedrally coordinated. We successfully measured aluminum edges with suitable statistics and sampling of the explored temperature range. Preliminary results of spectra obtained during the steaming reaction are shown in Figure 1. Al L-edge was recorded during the steaming reaction showing a clear variation in the pre-edges/L-edges intensity ratio with the steaming temperature, which is related to the dealumination process of the zeolite. This was confirmed by our simultaneous XRD measurements, illustrated in the inset of figure 1, where the main diffraction peaks of the zeolite are shifted to higher 2θ angles and decrease in intensity. These changes in the diffraction patterns are due to shrinking and partial amorphization of the zeolite cages by the selective extraction of Al atoms from the framework. Despite these results clearly show the variation in the Al local environment, a more detailed analysis of the spectra is currently being performed.

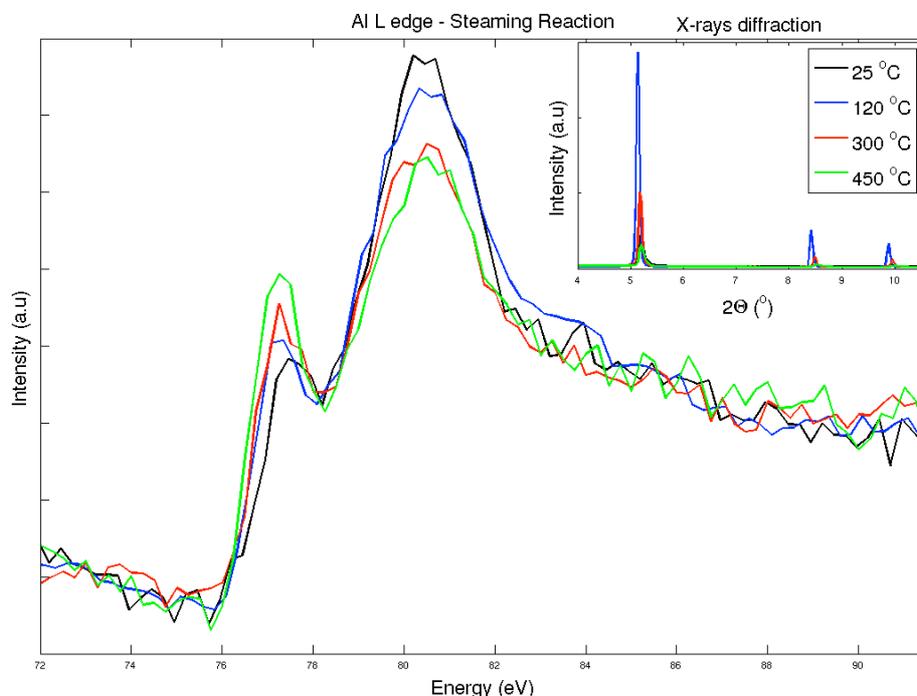


Figure 1: Al L edge measured during the steaming reaction at different temperatures (*main panel*) and corresponding X-rays diffraction (*inset*).

The second set of experiments were devoted to investigate the chemistry of the Al and C species during the methanol-to-olefins (MTO) reaction on zeolite H-Y and H-ZSM-5 by combining XRS, UV-Vis spectroscopy and mass spectrometry.

Al K- and L-edges and C K-edge were systematically investigated during in-situ MTO conversion with the aim of understanding the chemistry of the Al active sites and C-based species formed in the porous structure. In this case and due to the time resolution of the XRS measurements (0.5-1 h), we performed the reaction by adding pulses of methanol and subsequent collection of the XRS.

Despite these limitations, reliable data were obtained of the carbon K edge. We explored the progress of the methanol conversion reaction in two operative conditions ($T=350, 450$ C). Preliminary observation of these results are in agreement with the UV-Vis data, where the formation of carbonaceous species filling the porous structure of the zeolite can be observed and those increase with the progress of the reaction. A more careful treatment and analysis of these results is currently in progress.

A precise map of the C formation during first few minutes of the catalysis was, unfortunately, not possible to complete within this experimental timescale. Additionally, the chemistry of those carbon species in other MTO relevant systems was not explore due to the limited time. The promising results encountered in these beamtime suggests that is timely to apply now for more beamtime for the continuation of these promising experiments. The data of this performed experiment is currently being analysed in further detail and will be planned for a rapid publication.