ESRF	**Experiment title:** Structural study of Cu(II) ion migration in SSZ-13 zeolites	**Experiment number**: CH-4193
Beamline: BM01B	**Date of experiment**: from: 4 Dec. 2014 to: 9 Dec. 2014	**Date of report**: 7 Sep. 2016
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Report:

We proposed to study the migration of Cu-species in the chabazite (CHA) framework of the SSZ-13 zeolite using a combination of high-resolution powder X-ray diffraction (HR-PXRD), 2D powder X-ray diffraction (2D-PXRD), and X-ray absorption spectroscopy (XAS), namely extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES).

We performed XANES and 2D-PXRD during heating, cooling, and in between. Due to thermal effects and the desire to use Rietveld/maximum entropy method (MEM),[2] which demands a high signal-to-noise-ratio, HR-PXRD patterns had to be collected at lowest possible temperature, which at the given setup was room temperature (RT) for 6 hours. Full EXAFS scans were only measured in the beginning of the beam time, since the focus was on HR-PXRD, while XANES scans allowed immediate confirmation of the state of the sample, as discussed below.

The heating and cooling was very successful for all performed experiments. CHA zeolite is extremely hygroscopic and even trace amounts of water in the gas flow will coordinate to the Cu-species during the required 6 hour data collection.[3] The complete absence of water in the zeolite is essential for the successful characterization of extra-framework species, the goal of our beam time. After careful leak checking, we identified that the valves in the gas-flow system allow trace amounts of water to enter the system. After days of attempts we solved this issue by inserting a tube of dehydrated “sacrificial” zeolite sample in the flow system prior to the sample that was being measured. This allowed us to capture the trace water and to follow the hydration of the sacrificial zeolite, while making sure water did not reach the measured sample during the 6 hours of measurement. Thus, we succeeded in performing three complete experiments. For the first six experiments the HR-PXRD data were collected on gradually hydrating samples, and the data does not allow detailed analysis. It should also be mentioned that we had requested a gas-bottle with 20% O_2/He, but the bottle we received was mislabelled and we never managed to identify the actual content, but unexpectedly our sample turned dark brown/black.

Heating and cooling the sample beautifully reveals the dehydration and known negative thermal expansion (NTE) of CHA zeolite by 2D-PXRD,[4] while the XANES scans show a clear dehydration and oxidation of the Cu-species to Cu(II). This is confirmed by comparison to known XANES spectra of dehydrated Cu(II) cations in a CHA zeolite.[1] An example of this can be seen in Figure 1, where XANES spectra from an O_2 activation experiment is shown along with the reference spectra mentioned above. The data from this beam time are the first three spectra (black, red, and green). They show the state of Cu just before heating, just after cooling, and after cooling and 6 hours of HR-PXRD, respectively. The latter seems of a less quality, which may be due to improper alignment of the sample after HR-PXRD. However, it shows that the sample is still O_2 activated after the HR-PXRD measurement.

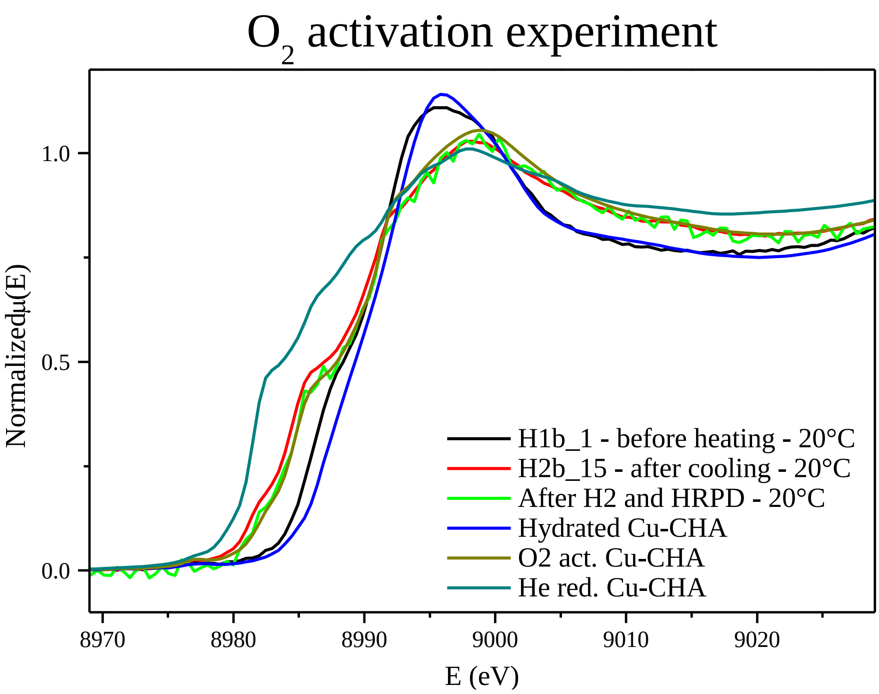

Figure 2: XANES spectra of an O_2 activation experiment. Before (black) heating and after (red) cooling, and finally after (green) cooling and doing HR-PXRD. The last three spectra are reference spectra from Giordanino *et al.*[1] Hydrated (blue), O_2 activated (brown), and reduced in He (teal) Cu-loaded CHA. The reference samples are similar to the one measured here.

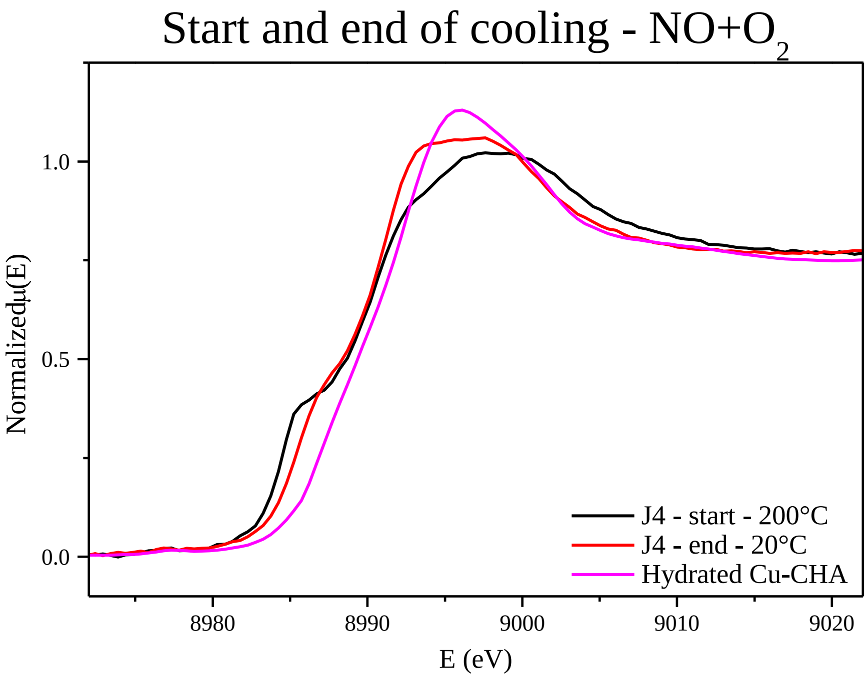

Figure 1: XANES spectra of the cooling from 200°C (black) to 20°C (red) in an NO+O_2 atmosphere. The last spectrum (pink) is a reference of a hydrated Cu-loaded CHA from Giordanino *et al*.[1]

This experiment was the first where we managed to keep the sample dehydrated throughout the HR-PXRD measurement.

In the final experiment we successfully treated the sample with a mixture of NO and O_2 after a pre-treatment with 10% O_2/He up to 300°C and then cooled down to 200°C. After some time at 200°C, the sample was cooled to RT whereafter the atmosphere was pure He during the HR-PXRD measurement. Figure 2 shows the XANES spectra measured at 200°C just before cooling (black) and just after cooling at 20°C (red). A reference spectrum (pink) is also shown of a hydrated Cu-loaded CHA, similar to the one in Figure 1. It can be seen that the complex that formed at 200°C disappears upon cooling. Figure 2 also shows it is possible a hydration is happening, however, it is evident that this is not the entire story. Furthermore, during the cooling the sample changed color from blue to yellow. The color change is determined by the coordination of the Cu cations. It seems the coordination rises, which is also evident in the rise of the white line of the XANES spectrum upon cooling. But whether the coordinating species are water or other species is to be determined. This will hopefully become clear from further analysis of the XANES spectra combined with the 2D-PXRD and especially the HR-PXRD, which may provide insight into the vailidity of multiple coordinating species upon Cu. In the end, if we wish to observe the complex that was sought after in this particular experiment, we will have to conduct HR-PXRD at 200°C. This will be tolerable only as long as the data is of a proper quality.

References

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[4] Woodcock, D. A., Lightfoot, P., Villaescusa, L. A., *et al.*, *Chemistry of Materials* **1999**, 11, 2508.