



	<b>Experiment title: Understanding the deactivation mechanisms of FCC particles and extrudates by heavy metal poisoning using confocal micro-XANES</b>	<b>Experiment number:</b> 26-01-985
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 12.02.14 to: 17.02.14	<b>Date of report:</b> 10.6.14
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**Names and affiliations of applicants** (\* indicates experimentalists):

Dr. Gareth Whiting\* (Utrecht University, The Netherlands)

Dr. Marleen Kerssens\* (Utrecht University, The Netherlands)

Prof. Bert. Weckhuysen (Utrecht University, The Netherlands)

Pieter Tack\* (Gent University, Belgium)

Prof. Laszlo Vincze (Gent University, Belgium)

Dr. Dipanjan Banerjee (Dubble beamline, ESRF, France)

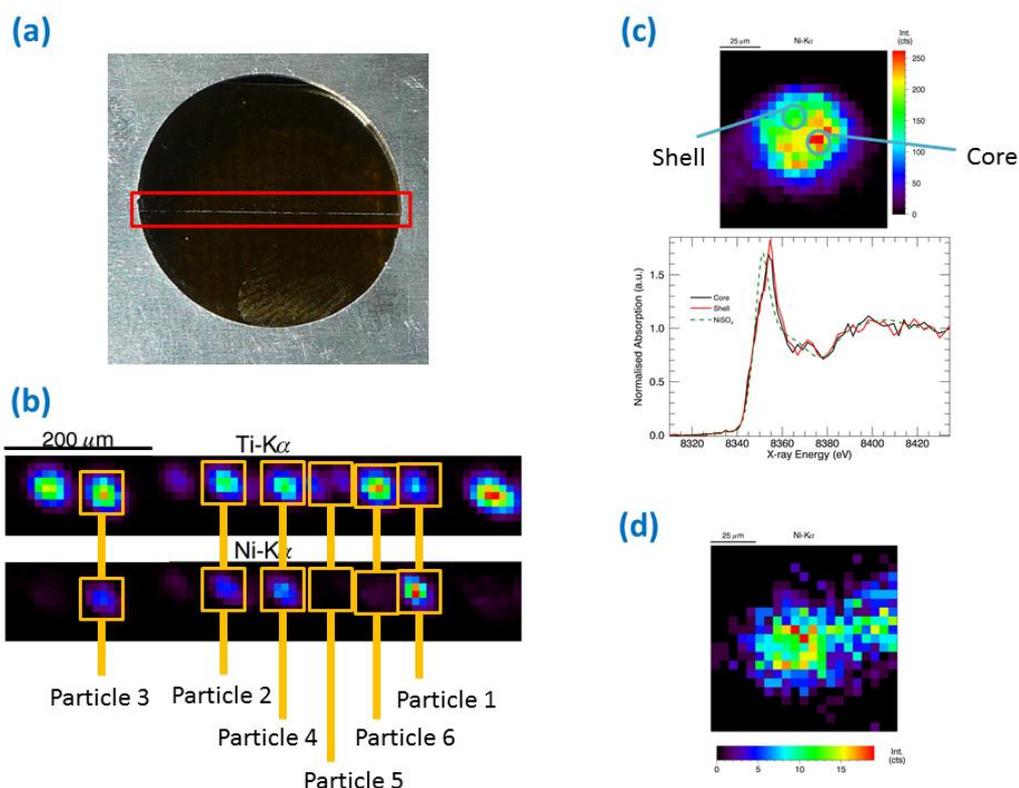
**Report:**

The aim of this beamtime proposal was to investigate both Fluid Catalytic Cracking (FCC) particles and zeolite containing extrudates, varying in level/species of poisoning, with non-invasive confocal micro-XANES, creating a 2-D and 3-D map of the distribution of poisoning in such materials. Ex-situ experiments were carried out to give unique insight into the distribution of metal poisons on these types of materials, combined with chemical information (oxidation and coordination state) about such elemental species, mimicking the conditions of the FCC process.

*1. FCC particles*

Ex-reactor FCC particles (containing high level of poisons) were used to obtain information about the distribution of Ni within not only a single particle, but in several particles. In order to perform novel confocal XANES (X-ray Absorption Near Edge Spectroscopy)/XRF (X-ray Fluorecence) scans on a series of FCC particles, a single line of particles were carefully mounted on kapton tape, supported by an aluminium holder (Figure 1a). Particles were investigated by XRF spectroscopy, by scanning slices throughout the particles. In Ni containing particles, a XANES scan (confocal volume  $\sim 20 \times 20 \times 20 \mu\text{m}^3$ ) was performed in shell and core regions to determine Ni oxidation state and chemical species.

Figure 1b displays the Ti and Ni XRF chemical maps for 6 FCC particles simultaneously. It is clear that the distribution/content of the Ni poison is not identical in each particle. However, further detailed analysis was performed in order to clarify these discrepancies. The XRF chemical map (100 x 100  $\mu\text{m}^2$ ) of particle 1 is depicted in Figure 1c. The Ni content appears to be located just off centre of the particle, with a limited amount at the shell. The corresponding XANES scan attributes the Ni content at the shell and the core both to  $\text{Ni}^{2+}$ , however the exact species is unknown (did not correspond with reference compounds). The XRF maps of the five other particles (Figure 1b) displayed a much lower content of Ni, an example of which is presented in Figure 1d, corresponding with particle 3. The Ni content was too low to attempt a XANES scan, however, it is clear the Ni distribution is different than in particle 1, where the most intense Ni seems to be at shell region.

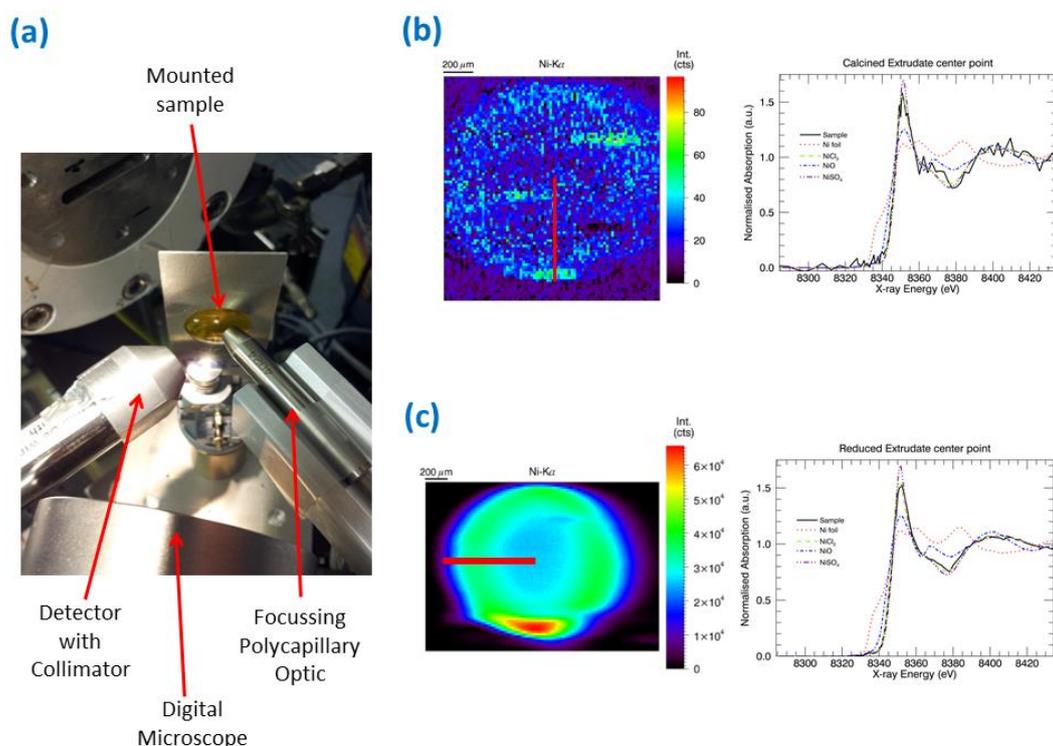


**Figure 1:** (a) Mounting of single line of FCC particles on kapton tape for confocal XANES/XRF measurements; (b) XRF scan showing distribution of Ti (top line) and Ni (bottom line) in several FCC particles. (10  $\mu\text{m}$  steps size in X and Y direction); (c) XRF map (100 x 100  $\mu\text{m}^2$ ) of particle 1 with corresponding XANES scans (red line: shell, black line: core); (d) XRF map of particle 3.

## 2. Ni/zeolite based extrudates

Two Ni/zeolite extrudate cross-sections of  $\sim 300 \mu\text{m}$  thick (one calcined and one reduced), were investigated using XRF mapping followed by Ni XANES scans, to determine the distribution of Ni in each sample, and also the species present. Figure 2a presents the experimental setup of the XRF mapping, showing the extrudate mounted on kapton tape, supported by an Al holder. Firstly, the calcined Ni/zeolite was investigated (Figure 2b). It appears that elemental distribution intensities drop off to the right hand side the extrudate, most probably due to thickness effects, however, some hot spots in Ni can be perceived. It can be stated tentatively that Ni is pronounced at the shell region of the extrudate cross-section, although the data is rather noisy. The corresponding XANES line scan of the sample

was compared with known reference compounds, Ni foil, NiSO<sub>4</sub>, NiCl<sub>2</sub> and NiO (Figure 2b). Although the spectrum is particularly noisy, it seems to correlate mostly with NiCl<sub>2</sub> (or a similar compound), with the edge position pointing towards Ni<sup>2+</sup>.



**Figure 2:** (a) Experimental setup showing extrudate cross-section (~300  $\mu\text{m}$  thick) mounted on kapton tape, supported by Al holder; (b) XRF map and corresponding XANES scan of calcined Ni/zeolite extrudate; (c) XRF map and corresponding XANES scan of reduced Ni/zeolite extrudate. (Legend in XANES scans: black line = sample; red line = Ni foil; green line = NiCl<sub>2</sub>; blue line = NiO; purple line = NiSO<sub>4</sub>)

The XRF map and corresponding XANES scan of the reduced Ni/zeolite extrudate cross-section is observed in Figure 2c. It is evidently clear that although both reduced and calcined samples contain the same Ni content, that the Ni signal here is significantly higher in intensity. This could be due to a heterogeneity between samples in the reduced batch, where some extrudates could contain a higher Ni content than the expected value. Also clear, is that a shell distribution of Ni is present, with the core containing a limited amount. The XANES spectrum is much more intense and can be assigned to NiSO<sub>4</sub> or a similar compound, with the edge position pointing interestingly to Ni<sup>2+</sup>. This suggests that although the sample has been reduced, its exposure to air has oxidised the sample.

In conclusion, it can be said that novel confocal XRF/XANES scans of several FCC particles is a promising method to evaluate poisoning in more than one particle simultaneously, showing that each particle contains a different distribution of Ni. Previous literature results focus only on one particle, where evidently, this is no longer accurate enough. XRF/XANES investigations of Ni distribution and species present in millimeter sized extrudate cross-sections also showed that this technique can be applied to larger scale materials, observing clear differences in distribution of Ni between calcined and reduced samples.