

Beamline report: CH5191

Novel, well defined Fe clusters grafted on SiO₂ for elective methane conversion to methanol: physical and electronic structure using XAFS, HERFD, and V2C XES.

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Our experimental work was significantly hindered due to technical issues of the beamline, namely breakdown of LN₂ cooling system of monochromator, followed by a crack of a silicon crystal analyzer chosen for XES measurements, due to which 3 days of the beamtime were lost and we were unable to carry out XES measurements as no suitable replacements were available. Responsible authorities offered us compensation for the time lost. Beamline staff provided us with significant help from all possible sides.

Remaining experimental time (11 shifts) of the beamtime was used in accordance with our proposal, where 3 shifts were spent on setting up the beamline, measuring relevant standard samples (FeO, Fe₂O₃, Fe, FeN_x, FeSi_x, FeCp₂) and evaluating risk of beam damage, which is of a great importance given by the long measurement times associated with requested techniques. Our measurements have shown that risk of beam-damage is relatively low as only in one case beam-induced reduction of Fe(III) to Fe(II) was observed. Following 5 shifts were dedicated to HERFD-XANES measurement (see details in following paragraph). Last 3 shifts were due to technical reasons reallocated to RIXS experiments upon discussion with our local contact in order to yield complementary info about electronic structure and to provide a solid base for rescheduled XES experiments (June 2018) and related modelling and simulation of XES spectra.

For the first time Fe K-edge HERFD-XANES measurements were recorded on well-defined silica-supported iron catalysts with low metal content (0.5 – 2 wt %). Measurements proved to be very demanding, as these low-concentrated samples required up to 5 hours per HERFD spectrum and 10 hours per RIXS map. Preliminary data analysis together with comparative approach indicates that a molecular species on the surface through grafting significantly alters LUMO structure of the iron center (see Figure 1). This can be explained through three related phenomena: spin state change, deviation from the centrosymmetry and changes in the ligand field. Our observations indicate, that the symmetry of the iron center might experience distortion due proximity of the surface and further changes are also induced by replacement of one of the ligands by surface silanol group, which bears less electron density than corresponding TBOS ligand. Spectra of the grafted species also shows significant edge-shift, which can be ascribed to formation of charge-transfer interaction. When the adsorbed species get involved, situation gets even more complicated due to additional changes in the structure. Detailed analysis of the data is ongoing, where modelling of structures will allow us to correlate pre-edge features with LUMO.

Aforementioned experiments validated the necessity of the HERFD-XANES measurements for well-defined systems. For the first time ever we got data about changes in

the pre-edge structure, occurring due to surface deposition and ligand removal/ligand addition. These changes are often ignored, as conventional XANES does not suffice to resolve them, but they pack highly important information about electronic structure of the metal center, which helps us to shed a new light on the fundamental process such as grafting of organometallic substrate on the surface of the support. EXAFS and XES measurements were from aforementioned reasons

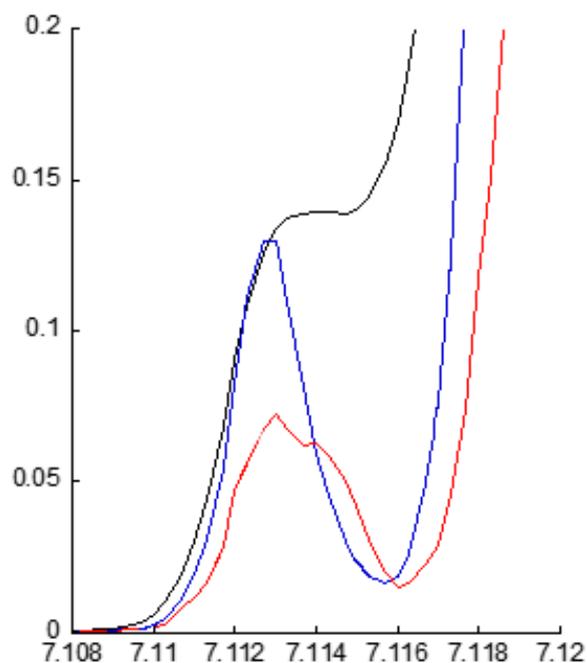


Figure 1. Comparison of pre-edge region of HERFD-XANES Fe K-edge spectra of four different samples: Fe(II) oxide (black curve), Fe(II) siloxide dimer (blue), Fe(II) grafted on the surface of partially dehydroxylated silica.

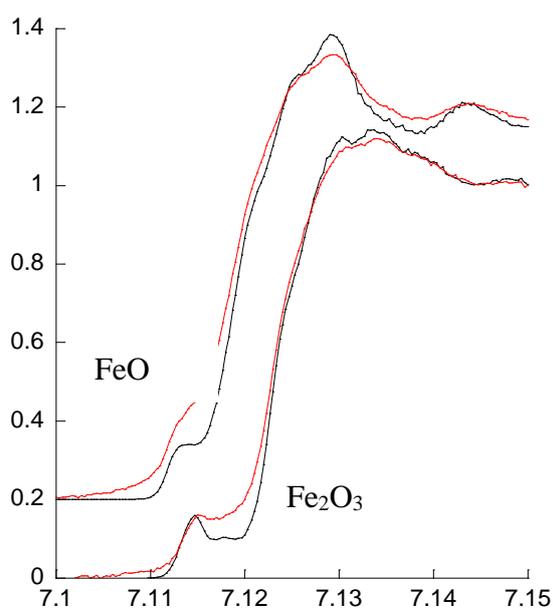


Figure 2. Comparison of HERFD-XANES Fe K-edge spectra of two standard samples, demonstrating the ability of the method to resolve weak structure. Red spectra belong to the total fluorescent yield (TFY), while black spectra belong to the HERFD data.

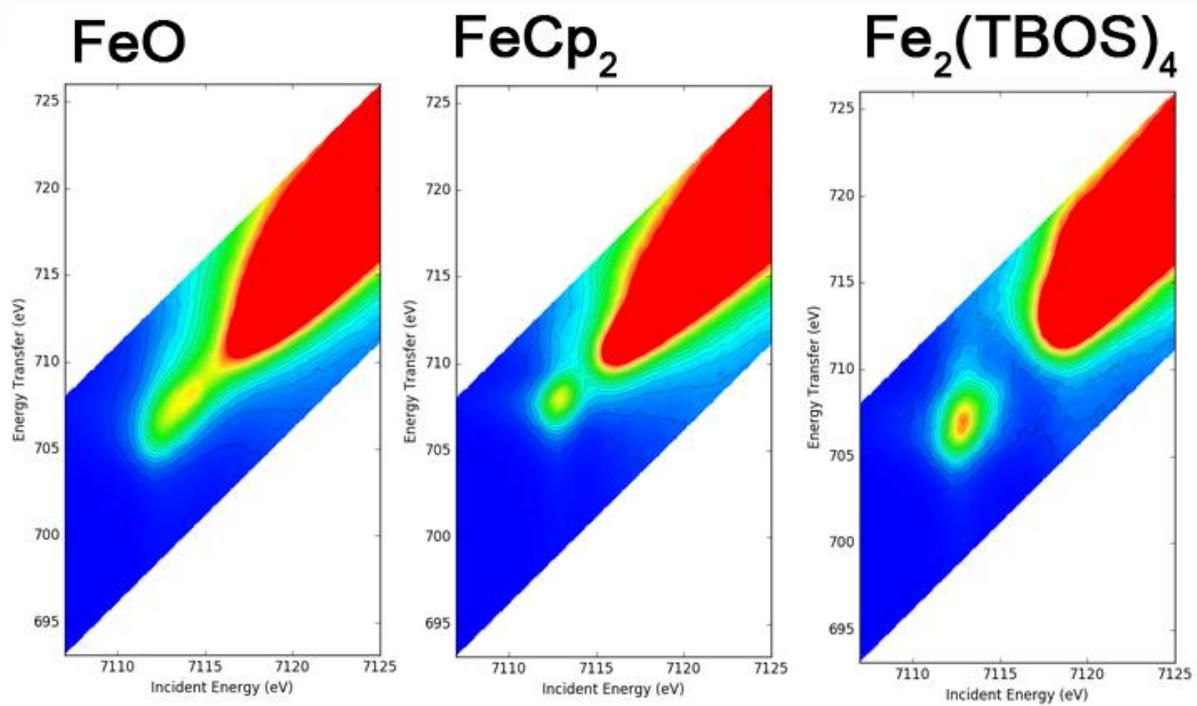


Figure 3. Comparison of RIXS Fe K-edge maps ($K\alpha$) of three standard samples, where very different transitions can be observed despite the same oxidation state; $Fe_2(TBOS)_4$ exhibits significant elongation along energy transfer axis; FeO has a maximum distributed very strongly along constant emission energy axis. $FeCp$ has weak and very well defined pre-edge feature without major asymmetries. FeO bears octahedral geometry, $Fe_2(TBOS)_4$ maintains symmetry of distorted octahedron and $FeCp_2$ (i.e. metallocene) has D_{5H} symmetry (in case staggered conformation is adopted).