

BEAMTIME REPORT

HERFD-XANES/RIXS study of structural and support effects on silica-based materials with single iron site for C-H activation of hydrocarbons (CH-5647)

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This beamtime was dedicated to Fe *K*-edge HERFD-XANES and RIXS measurements on air-sensitive silica-supported catalysts with iron single sites, used for the activation of C-H bond of methane. Our preliminary experiments at BM20 indicated that these X-ray techniques can provide us with a detailed insight into the electronic structure of the iron sites, unmatched by conventional XANES.

Approximately one half of the allocated time was used on gathering Fe *K*-edge HERFD-XANES spectra under normal conditions, while the second half was dedicated to RIXS and HERFD measurements using liquid helium cryostat. The measurements of the silica-supported samples were complemented by gathering spectra of reference samples with a variety of geometries, spin-states and oxidation states, such as iron(III) nitrate, iron(III) and iron(II) oxides, ferrocene, iron(II) chloride, iron(II) phtalocyanine, and iron siloxides. For selection of the reference spectra, see Figure 1.

The measurements proved to be demanding, as a multitude of samples was decomposing already after a short exposure to the X-ray beam. Among such samples, were dominantly ones based on iron(III). Application of the thinnest possible aluminium filter led to loss of 90 % of the signal intensity, drastically prolonging the measurement time needed to obtain reasonable S/N ratio. Cooling with cryostat partly decreased the radiation damage, but ultimately the frequent position-changing was necessary. Such a solution was non-trivial given by the fact that samples were presented in the form of sealed capillaries. Figure 2 shows time-resolved decomposition of iron(III) siloxide (grafted on the surface of silica) after exposure to X-ray beam, while using an aluminium filter. Already after two minutes, position of the edge shifts significantly to the lower values, indicating ongoing reduction process.

Figure 3 compares the XANES spectra recorded for the molecular precursor, silica-grafted species, and thermolyzed species. The loss of intensity and appearance of multiple features in the pre-edge of the grafted species indicate the presence of multiple iron sites, differing likely by their geometry. The oxidation state remains unchanged, although the position of the edge shifts about 0.8 eV higher, possibly due to the formation of electron-withdrawing interaction, such as meta-to-ligand charge-transfer. After thermolysis at 600 °C, the pre-edge region loses high-energy feature, indicating further changes of the geometry of iron centers. More rigorous analysis is ongoing (pre-edge fitting, variogram) and will be complemented by computational studies.

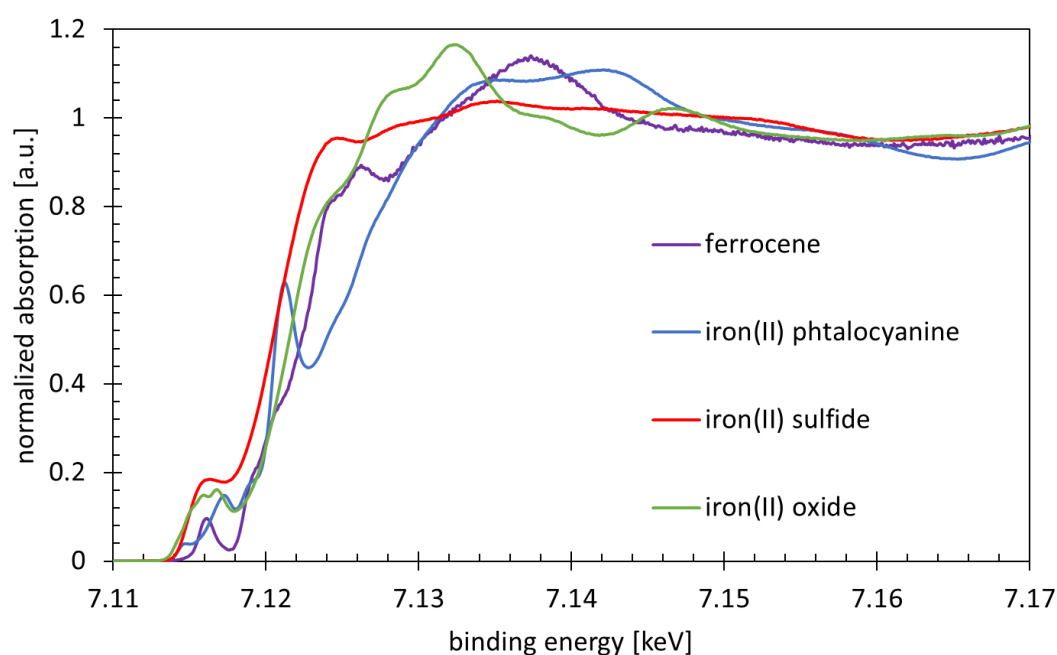


Figure 1. Iron *K*-edge HERFD-XANES spectra of the reference samples.

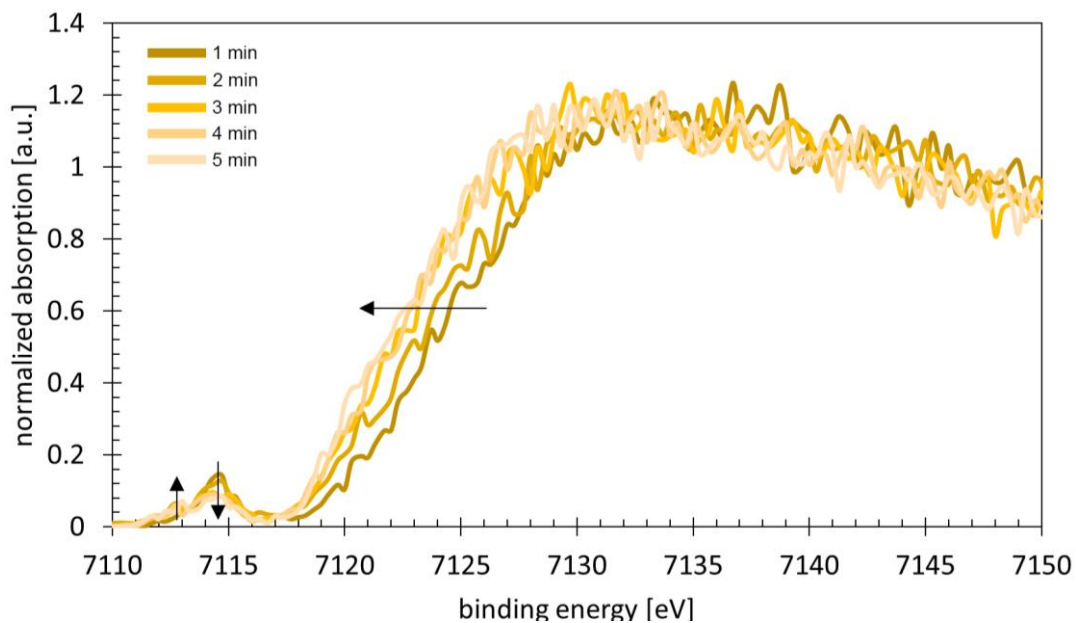


Figure 2. Time-resolved Fe *K*-edge HERFD-XANES spectra of iron(III) siloxide grafted on the surface of a silica partially dehydroxylated at 1080 °C, showing the beam-induced damage within the first 5 minutes after exposure to X-rays.

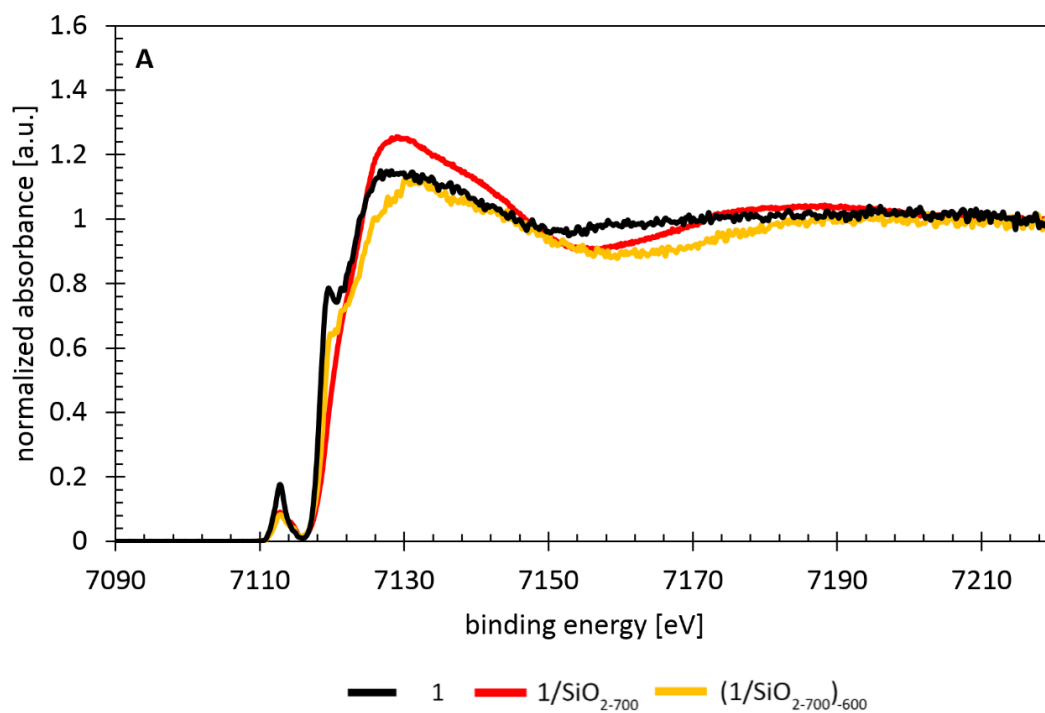


Figure 3. Fe *K*-edge HERFD-XANES spectra of iron(II) siloxide (labelled as 1), grafted species on partially dehydroxylated silica ($1/\text{SiO}_{2-700}$), and material thermolyzed in a vacuum at 600 °C, i.e. $(1/\text{SiO}_{2-700})_{-600}$.

