

**Experiment title:**

Impact of tungsten speciation on the catalytic selectivity during methane dehydroaromatization as revealed by operando X-Ray spectroscopies

Experiment number:**16-01-794**

Beamline: 30B	Date of experiment: from: 25 Jul 2018 to: 30 Jul 2018	Date of report:
Shifts: 15	Local contact(s): Antonio Aguilar, Olivier Proux	<i>Received at ESRF:</i>
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Preliminary note:

The initial proposal was dedicated to the characterization by HERFD-XANES and vtc-XES spectroscopies of the tungsten metal in the catalytic conditions of methane dehydroaromatization. Unfortunately, the BM16 beamline line suffered from technical problems before the run. The work program was change to another iron-based system used for the same reaction but more adapted for the BM30B line which is dedicated to standard XAS.

Report:

All Fe/ZSM-5 catalysts are prepared at TU Delft by classical impregnation. The operando XAS study relies on the use of a new catalytic set-up developed with FAME team for the study of gas phase catalytic reaction. On the spectroscopy side, the Fe K-edge XAS is recorded in fluorescence mode using the $K\alpha$ emission line. The initial state of the catalyst was characterized at room temperature and atmospheric. For Mo/HZSM-5, it is well known

that the oxidic catalyst precursor undergoes reduction and carburization at reaction conditions and can only activate the reaction of methane to benzene and naphthalene after completing this so called 'activation period'. It was suggested that Fe also has to undergo such a carburization to develop its activity. To verify this and to better understand the final structure of the Fe active site, *operando* XAS experiments were performed and the data analyzed by multivariate curve resolution (MCR) analysis.

In order to achieve good time resolution and to be able to compare the results with previous experiments performed on Mo/HZSM-5, a pulse-reaction technique was employed. With this technique, the point at which benzene starts forming and with that the moment when Fe has fully transformed to an active species can be determined exactly and a XANES spectra can be measured. Comparing this spectrum to known carbidic compounds, no match could be found. To determine the exact nature of the active Fe species is difficult, because the structure Fe takes on the support is different from a bulk iron carbide. Rather, Fe forms small cluster species inside the pores of the zeolite that are anchored by the framework Al as is shown by Py IR as well as nanoparticles on the outer surface of the zeolite crystal. Also, after exposure of the catalyst to reaction atmosphere, a mixture of Fe species with varying degree of reduction and carburization is formed. Thus, the measured spectra represent a mixture of spectra of pure components.

MCR analysis is a powerful technique to deconvolute multivariate systems and was used here to get more insight on the degree of carburization by determining the principal components describing the measured spectra. To reliably detect all the components, MCR was performed on XANES spectra recorded *operando* during several reaction treatments: He-treatment, methane pulsing to the He-treated catalyst, CH₄-TPR, CO-treatment, pulsing after CO treatment and H₂-treatment. It was found that four components can reasonable fit all 378 spectra. The MCR alternating least squares (MCR-ALS) routine yields the contribution of each component to the *operando* spectra (Figure 1). Comparing the theoretical spectra of the four components to spectra of reference compounds and with knowledge of the corresponding process conditions, their nature can be determined. Component 1 corresponds to the initial state of the catalyst, as the theoretical spectra of component 1 and the spectra taken of the catalyst prior to any treatment are very similar (Figure 1). Prior to any treatment, Fe is in a mixture of hematite (Fe(III), α -Fe₂O₃) and magnetite (Fe(II,III), Fe₃O₄) (Figure 1). Upon heating in He, the catalyst reduces until it is mainly made up of component 2, which closely resembles wüstite (Fe(II), FeO). Component 2 also forms during CH₄-TPR and CO-TPR while it is most dominant during the H₂-TPR at 470 °C. After reduction to Fe(II), component 4 is formed. Finally, benzene formation starts after the 17th pulse of methane has been sent to the reactor. At this point, component 3 dominates the spectra.

After benzene starts evolving at pulse 17, the catalyst slightly reduces further, but reaches a stable level soon after (Figure 1). This last reduction step does not translate to a higher benzene formation rate. Looking at the composition of the Fe/HZSM-5 catalyst after CO-treatment and considering that higher levels of benzene are achieved on this catalyst, it seems that retaining a certain amount of oxidic phase (component 2, FeO) is beneficial. Improved catalytic performance after applying the CO-treatment coincides with a higher concentration of component 2 (Figure 1).

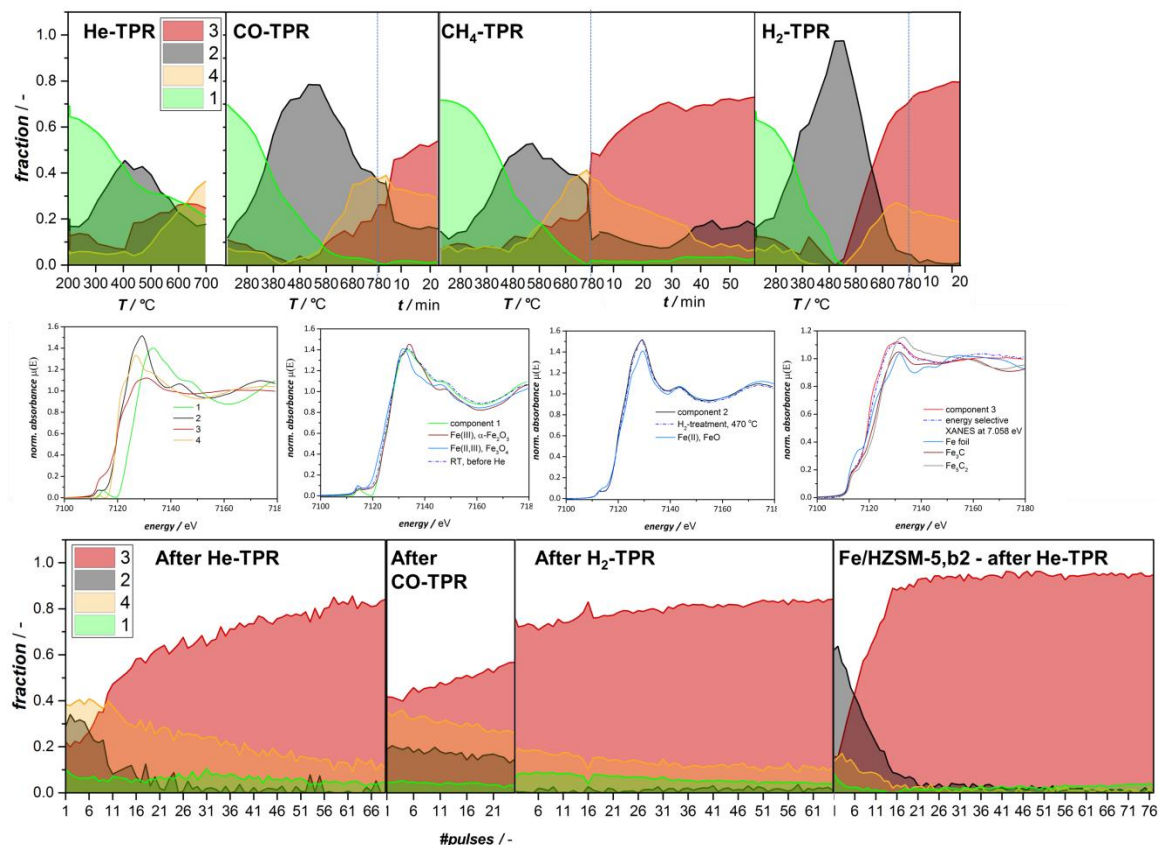


Figure 1. Concentration profiles of the four Fe-species found using the MCR-ALS routine on XANES spectra measured during different treatments applied to Fe/HZSM-5 or Fe/HZSM-5,b2.

A publication for Fe/ZSM5 catalyst is in preparation. Related works with Mo/ZSM5 catalyst is published:

A site-sensitive quasi-in situ strategy to characterize Mo/HZSM-5 during activation

Vollmer, I, Kosinov, N, Szécsényi, Á., Li, G., Yarulina, I., Abou-Hamad, E., Gurinov, A., Ould-Chikh, S, Aguilar-Tapia, A., Hazemann, J.-L., Pidko, E., Hensen, E., Kapteijn, F., Gascon, J., *Journal of Catalysis*, **2019**, Pages 321-331

On the dynamic nature of Mo sites for methane dehydroaromatization

Vollmer, I., Van Der Linden, B., Ould-Chikh, S., Aguilar-Tapia, A., Yarulina, I., Abou-Hamad, E., Sneider, Y.G., Olivos Suarez, A.I., Hazemann, J.-L., Kapteijn, F., Gascon, J., *Chemical Science*, **2018**, Pages 4801-4807