	Experiment title: In situ XAS study of metal modified HZSM-5 in bioethanol conversion	**Experiment number**: **26-01-1028**
Beamline**:** BM26A	Date(s) of experiment : 15/04/2015 – 20/04/2015	**Date of report**: -06-2015
Shifts: 15	**Local contact(s)**: Alessandro Longo, Dipanjan Banerjee	

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Summary

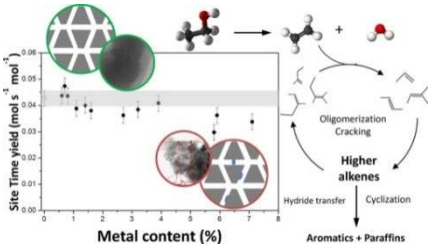

Figure 1: *The effect of metal content (Fe, Ga) on catalyst performance*[1].

The effect of metal modification (1 and 3wt% Fe and Ga) of zeolites by various synthesis methods was studied: (1) **incipient wetness impregnation (IMP)**, (2) **ion-exchange (IE)**, (3) **atomic layer deposition (ALD)** and (4) **isomorphic substitution (ISO)**. To investigate the structural changes leading to improved activity (from our previous study, Figure 1) XAS measurements were performed to study the local environment of Ga and Fe in zeolites during calcination and bioethanol conversion. The structural and electronic changes of the Fe and Ga species were verified in situ in different reactive atmospheres, which mimic the conditions in bioethanol conversion. Analysis of XANES measured during treatment / EXAFS recorded after treatment and subsequent modeling will provide structural details about the arrangement and location of atoms around the absorber.

Experimental conditions

XAS measurements were performed at the Fe K-edge (7112 eV) and Ga K-edge (10367 eV) in transmission mode. The properties of metal modified ZSM-5 were investigated during reduction (H_2/He till 650°C), oxidation (O_2/He till 550°C) and reactive steps (ethylene reduction and ethanol dehydration up to 450°C). In situ XANES was performed to follow the oxidation state changes during these treatments. Further, EXAFS scans were recorded before the reaction and at selected stages of catalyst treatments (after reduction, reaction and reoxidation). Hereafter, some examples of experiments and preliminary results are included.

Experiments performed and preliminary results

In the first stage of experiments, Fe-modified ZSM-5 were tested for changes during reduction and reoxidation. The XAS spectra of all 4 representative samples were obtained and compared with references Fe_3O_4 and Fe_2O_3 for structural and oxidation state changes. In the XANES region (Figure 2) the pre-edge regions for 3wt%Fe(IMP)-ZSM-5 and 3wt%Fe(IX)-ZSM-5 show similar features to Fe_2O_3. Whereas 3-Fe(ISO)-ZSM-5 exhibits pre-edge features, which could be a combination of Fe_2O_3 and Fe_3O_4. For all three samples, these pre-edge features indicate that at least one of the tetrahedral sites is occupied by Fe^{III}.

The post-reaction XAS spectra of 3wt%Fe(IX)-ZSM-5 after H_2-reduction, C_2H_4 reduction, ethanol dehydration and O_2-TPO allow to follow the location of Fe at various stages. As a preliminary analysis, the XANES region (Figure 3) of these XAS spectra were employed to study the final oxidation of this sample. The reduction with H_2 led to the shift in the edge position to a lower energy indicating formation of metallic Fe or FeO. Similarly, the spectrum after C_2H_4 reduction shows a partial reduction

as indicated by the edge position. However, the spectrum after ethanol dehydration indicates incomplete reoxidation. The reoxidation with oxygen also results in partial reoxidation. The k-space spectra (Figure 4) of this material reveal that the spectra show features similar to references Fe_2O_3 and Fe_3O_4. A detailed linear combination analysis will yield the exact nature of the sample.

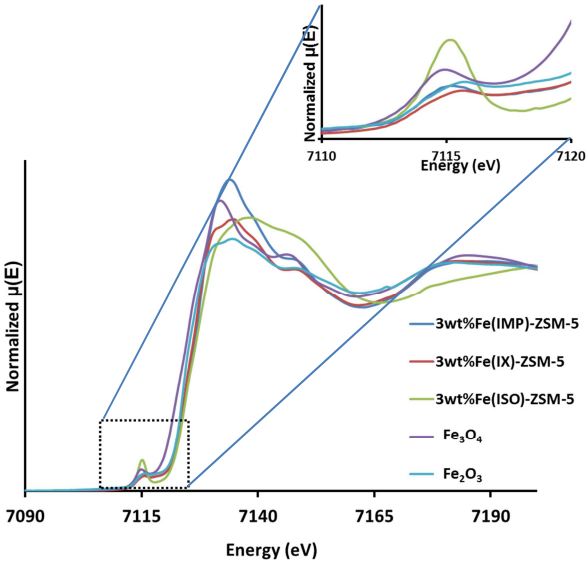

Figure 2: *comparison of various XANES spectra of 3wt%Fe-ZSM-5 as prepared by various synthesis routes with the references Fe_2O_3 and Fe_3O_4. Inset: zoom of the pre-edge features of the samples.*

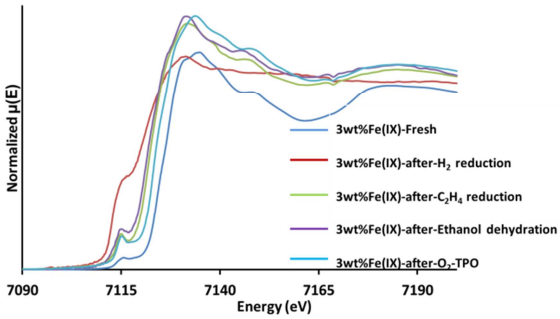

Figure 3: *The XANES profiles of the 3wt%Fe(IX) samples after various reactive treatments.*

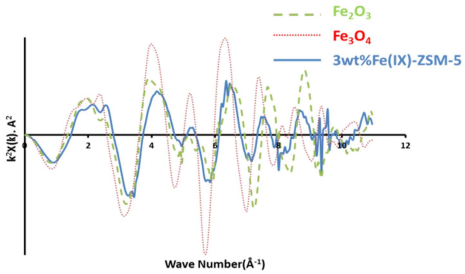

Figure 4: *k^2 weighted spectra of references and reoxidized 3wt%Fe(IX)-ZSM-5*

Similarly, changes during treatments of the Ga modified zeolites were identified for Ga(IMP), Ga(IX), Ga(ALD) and Ga(ISO)-ZSM-5. Interesting structural changes were identified especially during the reduction with H_2 and C_2H_4. The in situ profiles during H_2-TPR (Figure 5) show a decrease in white line intensity and shift in the edge energy indicating the reduction of Ga_2O_3. However, during cooling in H_2 the state of the material partially changed back towards Ga_2O_3 as indicated in the XANES spectrum in Figure 5.

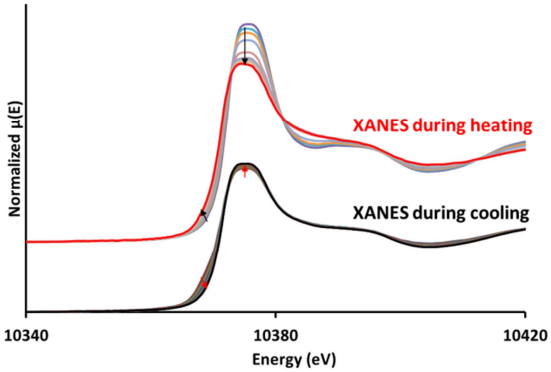

Figure 5: *In situ H_2-TPR profiles of 3wt%Ga(IX)-ZSM-5 from room temperature to 650°C and during cooling.*

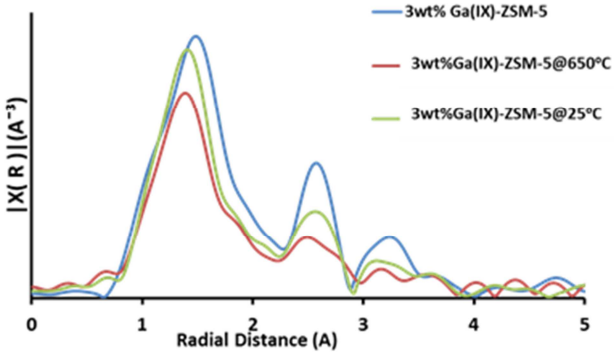

Figure 6: *R-space spectra of 3wt%Ga(IX)-ZSM-5 showing the Ga environment in the sample as prepared, after reduction at 650°C and back at 25°C.*

To pursue the changes in structure, full EXAFS measurements were performed at the maximum reduction temperature (650°C) as well as at room temperature after reduction (25°C). The R-space spectra reveal a decrease in amplitude of the first shell after reduction as indicated in Figure 6. However after cooling the structure remains close to the as prepared Ga_2O_3. Similar changes were obtained during the reduction with C_2H_4. A detailed EXAFS and in situ XANES analysis of Ga-modified ZSM-5 at various stages of reaction will help to get detailed insight in these structural changes.

References:

[1] Kristof Van der Borght, Vladimir V. Galvita and Guy B. Marin, Ethanol to higher hydrocarbons over Ni, Ga, Fe-modified ZSM-5: Effect of metal content, Applied Catalysis A: General, 492 (2015) 117–126.